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FINAL REPORT

Stream Sediment and Floodplain Soil Contamination in the Viburnum Trend in Crawford, Dent, Iron, Reynolds, and Washington Counties in Southeast Missouri

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EXECUTIVE SUMMARY

This study identifies the locations of mining-contaminated stream segments and quantifies the volume of contaminated sediment and lead mass storage in channel sediments and floodplain soils in streams draining mining operations in the Viburnum Trend (VT), including Big Creek near the Glover Smelter. Field work for this project occurred during the period from April 2012 to February 2013. Sediment samples for metals analysis were collected at a total of 124 different sites from VT streams and Big Creek. Metals analyses by X-Ray Fluorescence Spectrometry were completed on the <2 mm fraction of 889 sediment and soil samples including channel and floodplain areas and other landscape units. In addition, the <250 um sediment fraction for bed and bar samples was also analyzed for metals.

High concentrations of Pb and other metals were measured in stream sediments and floodplain soils in streams within 10 km of mining areas. Background concentrations of Pb in VT stream sediments not affected by mining tend to be <20 ppm for <2 mm fraction. Sediment Pb concentrations at levels five-times the Probable Effects Concentration (PEC) were found in Scoggins Branch, Crooked Creek, Lick Hollow, Adair Creek, Sweetwater Tributary, and Sweetwater Creek within 1 km below mine sites. To varying degrees, Pb-contaminated streams were contaminated with other metals including Zn, Cu, Co, and Ni. However, there were no streams contaminated with other metals that weren't also contaminated with Pb and Pb-contaminated lengths were always longer than or equal to other metals. The main findings of the study are:

- (1) More than 172 km of stream length were evaluated for Pb contamination during the screening phase. Based on Pb contamination >128 ppm Pb in the <2 mm fraction, a total of 42.1 km of stream length were identified as contaminated by mining operations in the Viburnum Trend and Big Creek. Lead concentrations in the <250 um fraction are elevated above 128 ppm for 57.9 km. Contaminated lengths of individual streams vary as expected according to stream size, magnitude of mining inputs, and watershed network factors that control sediment supply and dilution rates. Crooked Creek is contaminated over the longest distance at 13.5 km with Strother Creek the second longest at 5.3 km.
- (2) The highest channel sediment Pb concentrations measured in the <2 mm fraction are found in Adair and Sweetwater Creeks where the maximum concentrations frequently exceed 3,000 ppm. The lowest levels of contamination in VT streams at <200 ppm Pb are found in Neals-Left Fork Neals Creeks, Logan Creek below Sweetwater Creek, and Bee Fork. The proportion of finer sediment particles within bulk channel bed and bar sediments and their contribution to overall Pb burden in the sediment is variable and generally low. The percentage of <250 um particles in the <32 mm bulk sediment ranges from 2-3% in Crooked and Neals Creeks to a high of 40% in Sweetwater Creek and mine tributary. Thus, for some streams, contamination trends in the

- <250 um sediment fraction need to be evaluated within the context of their low overall abundance in channel sediment. Indeed, the percent of <250 um Pb mass relative to total Pb in the <2mm fraction is typically <30%;
- (3) Active channel width is the most significant predictor of channel sediment storage compared to other geomorphic variables such as slope, depth, elevation, and drainage area. Therefore, a geomorphic model is used to predict channel sediment storage for contaminated stream segments ($r^2 = 0.910$ for total storage x channel width regression equation). In general, total channel sediment storage decreases dramatically when active channel width is <20 m, reach elevation >300 meters above sea level, drainage area <15 km², and/or exposed bedrock covers >10% of the channel bed;
- (4) Logan Creek, Bills Creek, and Strother Creek were not found to contain contaminated floodplains using the methods of this study. For contaminated floodplains, the maximum depth of contamination observed was 0.5 m, but typically the depth of contamination was <0.3 m. Cesium-137 analysis indicates that the 1963 peak in Cs-137 occurs below the depth of the Pb peak in almost all cores analyzed. Therefore, contaminated sediment layers in these floodplains are of VT mining age;
- (5) Big Creek had the most contaminated floodplains in the VT. Floodplain contamination along Big Creek is likely related to aerial deposition of Pb from smelter operations at Glover. There is little contaminated channel sediment in Big Creek from areas upstream of Scoggins Branch. Therefore, floodplains along this segment were not contaminated from stream-derived sediment Pb, but from aerial deposition of Pb smelter emissions;
- (6) In the VT, total combined channel and floodplain storage of contaminated sediment is 997,000 m³ with 83% associated with in-channel deposits and the remainder in floodplains. About one-half of the contaminated sediment is stored in Crooked Creek, Bills Creek, and Sweetwater Creek. In these streams, in-channel storages typically represent >80% of the total contaminated sediment volume. Big Creek contains the highest volume of contaminated floodplain sediment storage due to past aerial deposition from the Glover smelter at 54,000 m³. The total mass of Pb stored within alluvial deposits in VT streams is 494 Mg with only 42% in channel sediments and 58% in floodplain soils. More than three-fourths of the Pb mass is stored in Big Creek, Crooked Creek, Sweetwater Creek, and Adair Creek. As expected, Big Creek contains the most Pb in floodplain storage at 137 Mg; and
- (7) The Logan Creek Watershed including Adair Creek, Sweetwater Tributary, and Sweetwater Creek is currently storing about one-half of the contaminated sediment volume and Pb metal mass within VT stream systems. While the active channel of Logan Creek is a sink for Pb and sediment delivered from upstream areas, contaminated sediment problems are relatively severe in Sweetwater and Adair Creeks since channel sediments tend to contain >2,000 ppm

Pb. The Logan Creek channel is contaminated between Adair and Sweetwater Creeks with Pb at concentrations typically ranging from 140 to 440 ppm with a maximum measured concentration of 615 ppm Pb.

(8) Contaminated sediment and Pb storage in floodplain deposits represent potential long-term sources of Pb contamination to riparian lands as well as the stream itself. Bank erosion and soil weathering can continue to release floodplain stored Pb to the stream for many decades after the mining has ceased.

INTRODUCTION

Missouri is the largest producer of lead (Pb) in the United States and generally ranks in the top five states in zinc (Zn) production (Seeger, 2008). The Viburnum Trend (VT), also referred to as the New Lead Belt, is the only Pb mining area currently active in the state. The VT is a subdistrict of the Southeast Missouri Lead Mining District (SEMOLMD) which has a productive history of Pb mining beginning in the 1700s near Potosi and Mine-LaMotte in Fredericktown, Missouri (Seeger, 2008). Deep shaft mining began in the SEMOLMD during the 1890s in Leadwood, Desloge, Park Hills, and Bonne Terre, Missouri within the Old Lead Belt subdistrict. The VT is located about 20 to 40 km southwest of the Old Lead Belt and covers about 500 km² of headwaters of the Black and Meramec Rivers in the Ozark Highlands which drain the Salem Plateau and St. Francois Mountains (Figure 1). As ore reserves became depleted in the Old Lead Belt, renewed ore body exploration efforts discovered high grade lead deposits in the VT in 1955. The first mine was opened in 1960 at Viburnum #27 Mine in Crawford County near Viburnum, Missouri. To date, 10 mines have operated in the VT along a north-south line extending for almost 100 kilometers (km) from Viburnum to Bunker, Missouri. Total ore production for individual mines in the VT ranges from 20 to >50 million tons with a metal content of 8% Pb and 3% Zn (Seeger, 2008). Two smelters were opened in 1967 to serve the VT, one near the Buick Mine in Boss, Missouri and the other in Glover about 35 km to the east.

There are ongoing concerns about where and how mining activities in the VT affect the quality of stream water, sediment, and wildlife habitat (Besser et al., 2007 & 2009; Allert et al., 2008 a & b; Stroh et al. 2009; Weber, 2012). About 14 km² of land and pond area have been directly disturbed and potentially contaminated by mining and milling operations (USFWS & MDNR, 2009). It was recognized early on that mining, milling, and smelting operations in the VT presented a metal contamination risk to local streams, soils, livestock, and wildlife (Hardie et al., 1974; Dorn et al., 1975; Wixson, 1978; Gale and Wixson, 1979; Jennett and Foil, 1979). Further, elevated concentrations of mining-related metals in runoff and sediment particles have been detected more than 30 km downstream from mining sites (Brumbaugh et al., 2007; Krizanich, 2008). Recent studies have reported that re-suspended road dust in areas contaminated with mining materials may present a health risk to local residents by atmospheric exposure (Witt et al., 2013 & 2014).

Government agencies have worked to identify and assess the risk of mining related contamination problems in the VT. Missouri's 2014 303(d) list contains 10 stream segments that are impaired by mining-related contaminants from VT mining and smelting operations including lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), and arsenic (As) in water and sediment (http://www.dnr.mo.gov/env/wpp/waterquality/303d.htm). The listed segments are found in the following watersheds: Indian Creek including a portion of Courtois Creek and Crooked Creek in the Meramec Basin; Strother Creek and Middle Fork in the middle fork of the Black River Basin; Bee Fork and West Fork in the west fork of the Black River Basin; Logan Creek in the Black River Basin, and Big Creek and Scroggins Branch in the St. Francois Basin. Total Maximum Daily Loads (TMDLs) have already been approved for Indian Creek and Big Creek with TMDLs currently under development for most of the other listed stream segments. Preassessment screen and determination reports have been released for several streams (USFWS, 2008; USFWS & MDNR, 2009). The Final Phase I Assessment Plan has also been released for Adair Creek, Logan Creek, Sweetwater Creek, Black River, West Fork-Black River, Big Creek, and Scoggins Branch (Mosby et al., 2009). Moreover, mitigation and restoration plans for the Bee Fork have been specified within the Doe Run Resources Corporation multimedia Consent Decree (USEPA, 2010).

The long-term environmental risk of contaminated sediment in mined watersheds is related to the volume and environmental mobility of contaminants stored in older channel and floodplain deposits as well as present-day mining source loads and their control (Miller and Orbock-Miller, 2007). Metal contaminants do not break down in the environment and therefore can be stored in alluvial deposits for decades to centuries to become available later to the stream during channel erosion or chemical weathering. In general, mining wastes become incorporated within natural sediment loads and therefore tend to be deposited and stored in both channel and floodplain deposits in mined watersheds (Lecce and Pavlowsky, 2001). In-channel deposits are typically composed of coarser sand and gravel sediments located below the bank top elevation of the active channel which is normally filled to capacity by floods once every year or two in Midwestern streams such as those in the Ozarks (Rosgen, 1996; Simon et al., 2004; Pavlowsky and Martin, 2010; Owen et al., 2011). As the channel migrates back and forth across the valley floor overtime, the areal extent of channel deposits can increase laterally by deposition of new bar material or decrease during erosion and reworking by higher flows. On the other hand, floodplain deposits are typically fine-grained and form when suspended sediment is transported across and settles on the valley floor during overbank flooding (Lecce and Pavlowsky, 2001). Channel bank erosion and floodplain surface scour by floods can release contaminated floodplain sediment back to the stream overtime. Nevertheless, floodplains can store metal contaminants for millennia (Miller and Orbock-Miller, 2007).

In general, there are three types of in-channel deposits that can store mining sediment in the VT. First, <u>bed deposits</u> occur on the bottom of the main channel thread and are saturated by

low flows most of time. Bed features including riffles and pools that are maintained by erosion and deposition on the channel bed during floods or high flows capable of transporting coarse sediment including sand, gravel, and cobbles (Rosgen, 1996) (Appendix A-Pictures 8, 9a, 13, & 14). Second, <u>bar deposits</u> form as thicker sediment bodies on the channel bed that are typically exposed during low flow conditions. Fluctuations of sediment supply and transport rates within the active channel during high in-channel flows and overbank floods produce the conditions for bar formation. The size and location of bar deposits are affected by channel pattern, slope, and sediment supply (Rosgen, 1996; Martin and Pavlowsky, 2011). The sediment size distribution of a bar deposit is usually coarsest near the bed and fines with elevation above the bed (Leeder, 1982). Sediment size can also decrease downstream within a single bar deposit with upstream bar heads typically being coarser than downstream bar tails (Rosgen, 1996).

Well-sorted channel deposits or those containing a narrow range of particle sizes typically have porosities ranging from 26% to 48% (Leeder, 1982). Therefore, finer-grained sediments, such as silt and clay particles, and associated contaminants can become trapped and accumulate within the pore spaces of coarse bed and bar materials. The degree to which fine sediment accumulates within pore spaces of larger bed materials is called embeddedness. Excessive embeddedness can negatively impact aquatic life by reducing the space and types of shelter available, restricting oxygen and nutrient cycling, and increasing the exposure to contaminated sediment for sediment-dwelling organisms (Sennatt et al., 2006).

Bench (or shelf) deposits are the third type of in-channel sediment deposit which can become contaminated by mining-related metals in the VT (Owen et al., 2011). Benches are often described as transitional features reflecting geomorphic changes in the channel over periods of years to decades due to variable discharge and sediment regimes. Benches can form as channel bars become buried by fine sediment over time, possibly to form new floodplains in the future. Stable bar surfaces become vegetated and increase fine-grained sedimentation rates as flow velocity is reduced by dissipation or deflection of hydraulic energy (McKenny et al., 1995). Benches can also form as channel banks adjust to subtle changes in flood and sediment regime over periods of years to decades (Davis, 2009).

The <u>purpose</u> of this project is to improve our understanding of the spatial distribution of sediment contamination and to quantify the volumes of stored mining-contaminated sediment in channel deposits and on floodplain soils in VT streams draining mining areas. In this study, contaminated channel sediments are defined as those containing at least 128 parts per million (ppm) of Pb in the <2 mm size fraction which is the probable effects concentration (PEC) used to indicate toxicity to sediment-dwelling organisms (MacDonald et al., 2000). Sediments are also defined as contaminated if they exceed published PEC values for other metals at 149 ppm for Cu, 49 ppm for Ni, and 459 ppm for Zn (MacDonald et al., 2000). In VT streams, metal burdens in stream sediments and floodplain soils tend to be concentrated in the finest sediment fractions which are also most available to sediment-dwelling organisms (Brumbaugh

et al., 2007; Femmer, 2008; Lee, 2008). Therefore, relationships between metal concentrations in the <2 mm and <250 um fractions and the influence of the finest sediment size fractions on Pb contamination and storage will also be evaluated including clay, silt, and fine sand fine sand in channel bed and bar sediments. However, only the <2 mm sediment fraction will be evaluated for bench-top and floodplain deposits since there is usually no need to sieve the samples further or analyze a finer fractions since the sediments are naturally fine. Further, bench-top deposits occupy higher topographic positions than bed or upper bar deposits and do not provide perennial aquatic habitat for sediment dwelling organisms.

Floodplain soils and bench deposits are affected by different drainage conditions and lower risk of biological toxicity compared to sediments in aquatic environments. In this study, contaminated floodplain soils and bench deposits are defined as those containing at least 345 ppm Pb in the <2 mm size fraction based on toxic effects to birds in the VT (Beyer et al., 2013, Holmes and Lipton, 2014). A previous study on the Big River used a floodplain soil threshold of 400 ppm Pb based on human exposure which was derived from EPA's residential yard cleanup guidance criteria in Region 7 (Pavlowsky et al., 2010a).

The objectives of this project are as follows:

- (1) Identify the location and length of mining-contaminated streams based on Pb concentrations in the <2 mm sediment fraction of >128 ppm in active channel sediments and >345 ppm in floodplain soils in streams draining mining areas in the VT;
- (2) Quantify the downstream distribution and volume of contaminated alluvial deposits including channel bed, bar, and bench deposits and floodplain soils at the reach- and watershed-scales; and
- (3) Evaluate streams based on the magnitude of storage of contaminated sediment, Pb mass, and Pb concentrations in both channel deposits and floodplain soils with an emphasis on sediment transport patterns and probable residence times.

MINING CONTAMINATION IN THE VIBURNUM TREND

Metal contamination is associated with finer sediment fractions in VT streams affected by mine and mill sources. Relatively high concentrations of mining-related metals have been released to local streams by tailings pond drains and outfalls, wind-blown dusts from tailings storage area, spillage along haul roads, and smelter fallout (Wronkiewicz et al. 2006; Seeger, 2008; Witt et al. 2013). These sources tend to contaminate relatively fine sediment fractions that are <63 micrometer (um) in diameter which are highly mobile in the stream environment and can bind metals to concentrations that are potentially toxic to aquatic life (Schmitt and Finger, 1982; Mosby et al., 2009). Therefore, the highest concentrations of metals are typically found in the fine-grained fraction within channel bed deposits, typically <250 um or smaller in diameter in

VT streams (Schmidt and Finger, 1982; Femmer, 2004; Wronkiewicz et al., 2006). Several studies in the VT involving a variety of field sampling and laboratory methods have consistently found that elevated concentrations of Pb, Zn, and other mining-related metals are transported in strong association with fine sediment particles and that toxic concentrations are frequently found in stream sediments and pore-waters within 10 km below mining areas (Jennett and Foil, 1979; Brumbaugh et al., 2007; Femmer, 2008; Lee, 2008; Hannon, 2012).

It is expected that the source and fate of sediment-metal contaminants in VT streams will differ from those found in the Old Lead Belt sub-district to the northeast. In the Big River and Flat River Creek in St. Francois County, mining-related Pb concentrations are distributed across a wider range of particle sizes ranging from silt to fine gravel (Pavlowsky et al., 2010a). Further, the mining history also differed between the two sub-districts (Seeger, 2008). In the Old Lead Belt, mining wastes were released directly to the river system from unstable mine dumps or mill outflows beginning in the 1890s, much earlier than the VT where the first mine opened in 1960. Mining chat composed of coarse sand and fine gravel sized material produced during gravity milling was released in relatively large amounts to the Big River until the early 1930s when flotation milling and tailings dams became common in the District. After introduction to the river channel, contaminated sediments were deposited within gravel bars and on floodplains to depths of 2 meters or more (Pavlowsky et al., 2010a). Finer-grained contaminated sediment continued to enter Big River throughout the active mining period from mill inputs and reworked mining sediment.

While the Old Lead Belt had a longer mining history with few environmental controls prior to World War II, mining contamination in the VT probably started around 1960 and modern environmental controls including managed tailings impoundments were in-place from the start (Femmer, 2008). Therefore, metal contamination in VT streams is primarily associated with point discharges of mine and tailings impoundment water (Kleeschulte, 2008b; Schumacher, 2008), storm runoff from contaminated land and road areas (Jennett and Foil, 1979), and aerial deposition from smelter stacks (Gale and Wixson, 1979). Accidental releases of contaminated mill wastes and tailings directly into nearby channels were rare, but did occur (Duchrow, 1983; Mosby et al, 2009). Another difference between the two mining districts relates to patterns of watershed contamination. Mining sites were located along the main stem of the Big River within the middle portion of the basin. However, mines in the VT were located along smaller and steeper headwater streams distributed among several watersheds feeding the Black and Meramec Rivers (Brumbaugh et al., 2007). Mining contamination problems in the Big River are largely associated with a single large main trunk river system draining 1,000 to 2,500 km², while sediment contamination in the VT occurs over several watersheds typically draining from 10 to 100 km² (Figure 2).

Mining-related Pb contamination of VT stream sediments was first recognized in the 1970s during studies by Missouri University of Science and Technology (then called the University of

Missouri-Rolla) (Hardie et al., 1974). Jennett and Foil (1979) measured Pb concentrations in mining areas ranging from 183 to 1,032 ppm in the <250 um size fraction of stream sediments collected from Indian Creek, Strother Creek, and Bee Fork, while background Pb concentrations <33 ppm were found in stream sediments above mining influence. Gale and Wixson (1979) evaluated the effects of ore processing and smelter inputs on sediment and water quality of Crooked Creek and described efforts by the mining industry to reduce contamination effects. More recent studies have focused on improving the understanding of mining impacts on elevated metal concentrations in stream water and sediment (Wronkiewicz et al., 2006; Brumbaugh et al., 2007; Lee, 2008; Hannon, 2012). Moreover, biological impairments in VT streams were related to elevated concentrations of Pb and other metals in fine-grained sediments and pore waters within coarse riffle deposits (Besser et al., 2007; Allert et al., 2008; Poulton et al., 2010).

The spatial extent of present-day Pb contamination in VT streams is generally known. However, it is important to accurately assess the longitudinal variation in measured Pb concentrations when trying to evaluate the sources and storage of mining-Pb in a watershed. Sediment Pb concentrations tend to decrease downstream below mining sources to background levels within 15 km or less in the headwater streams of the VT due to the effects of dilution by background sediment, sedimentary deposition, and biologic uptake (Brumbaugh et al. 2007; Lee, 2008). For example, sediment Pb concentrations in Strother Creek in the year 2004 decreased with distance below the Buick tailings pond dam (at 0 km) in the following order: 827 ppm at 5 km; 182 ppm at 8 km; 68 ppm at 12 km; and 28 ppm on the Middle Fork Black River immediately below the confluence at 16 km (Brumbaugh et al. 2007). Further, Pb concentrations in a sediment core from Clearwater Lake increased from an average of 37 ppm in the pre-mining period to an average of 79 ppm after the start of mining in the Black River basin in 1966 (Krizanich, 2008). While the lake is located about 60 km from the furthest upstream VT mine, it is believed that the source of enriched Pb in the core was from the Sweetwater Mine located about 30 km upstream in the Logan Creek watershed which started production in 1968 (Femmer, 2008; Krizanich, 2008). In general, background Pb concentrations in the <250 um fraction of sediments from streams not affected by mining, but still within VT watersheds, tend to be <20 ppm (Hannon, 2012). In contrast, maximum Pb concentrations in fine-grained (<250 or <63 um) stream sediments below VT mining operations can reach levels that are >100 times background levels (Femmer, 2004; Brumbaugh et al. 2007; Lee, 2008).

STUDY AREA

The Viburnum Trend (500 km²) is located in Southeast Missouri in the Ozark Highlands ecoregion (Figure 1). In total, about 153 km of stream length was evaluated for sediment contamination for this study as follows (Figures 2A to 2F):

- (1) <u>Indian/Courtois Creek Watershed (17 km)</u> including Indian Creek (13 km) and Courtois Creek (4 km) (Appendix A-Picture 12);
- (2) <u>Crooked/Huzzah Creek Watershed (25 km)</u> including Crooked Creek (16 km), Huzzah Creek (3 km), and Mill Rock Creek (6 km) (Appendix A-Picture 6);
- (3) <u>Strother Creek/Middle Fork of the Black River Watershed (37 km)</u> including Left Fork-Neals Creek (2 km); Neals Creek (10 km), Strother Creek (12 km); and Middle Fork-Black River (13 km) (Appendix A-Picture 1, 5, & 7);
- (4) <u>West Fork Watershed (48 km)</u> including Lick Creek (1 km), Bills Creek (5 km), West Fork-Black River (27 km), and Bee Fork (15 km) (Appendix A-Picture 3, 11, 15 & 16);
- (5) <u>Logan Creek Watershed (18 km)</u> including Adair Creek (2 km); Logan Creek (10 km); Sweetwater Creek (5 km); and a tributary to Sweetwater Creek (1 km) (Appendix A-Picture 8, 9, 10, 13 & 14); and
- (6) <u>Big Creek Watershed (8 km)</u> including Big Creek (7 km) and Scoggins Branch (1 km) (Appendix A-Picture 17 & 18);

Geology

Mining operations are located along the divide between the Meramec and Black River basins on the Salem Plateau and the western flank of the St. Francois Mountains. Viburnum Trend streams head in Ordovician dolomites and then flow across the Viburnum fault line over Cambrian dolomite. Chert nodules are a common constituent in the dolomite bedrock and thin discontinuous lenses of sandstone occur locally. The headwaters of Big Creek are underlain by Precambrian granite and rhyolite bedrock of the St. Francois Mountains near Taum Sauk and flow south over Cambrian dolomite in to the St. Francois River (Seeger, 2008).

Ore minerals in the VT are primarily hosted by bacterial stromatolite reefs and associated oolitic rocks of the Cambrian-aged Bonneterre dolomite. The primary ore in the VT is galena (Pb) with sphalerite (Zn) of secondary importance. Also of secondary importance, copper is produced from chalcopyrite and bornite ores. Of minor importance, cobalt and nickel are produced from siegenite and bravoite ores, sulfur from the iron sulfide, pyrite, and silver during the galena smelting process. The major gangue minerals in the VT are the carbonates dolomite and calcite, marcasite, another iron-sulfide, and quartz (Seeger, 2008). Deep shaft mining occurs in dolomite host rock with finely-disseminated galena ores processed in flotation mills located on-site or at other nearby mines. Mill tailings in the form of fine-grained mineral wastes were released from mills and stored in large ponds formed by dams constructed across stream valleys (Seeger, 2008).

Viburnum Trend Mining History

The New Lead Belt in southeastern Missouri has been a major producer of lead (Pb) and other metals since 1960 when the first mine opened in Viburnum, Missouri (Seeger, 2008) (Table 1). To date, 10 mines have operated along a north-south line extending for almost 100 kilometers (km) from Viburnum to south of Bunker, Missouri. This subdistrict of the Southeast Missouri Lead Mining District is referred to as the Viburnum Trend. Seven mines are presently in operation in the VT: (i) Viburnum #29 Mine in Washington County which uses the Buick Mill; (ii) Casteel or Viburnum #35 Mine in Iron County which uses the Buick and Brushy Creek Mills; (iii) Buick Mine and Mill in Iron and Reynolds Counties; (iv) Fletcher Mine and Mill in Reynolds County which sometimes uses the Brushy Creek Mill; (v) Brushy Creek Mine and Mill in Reynolds County; (vi) West Fork Mine and Mill in Reynolds County; and (vii) Sweetwater Mine and Mill in Reynolds County (Seeger, 2008) (Table 1 & Figure 1). In addition, three mines have been closed including Viburnum #27 Mine in Crawford County (1978), Magmont Mine in Iron County (1994), and the Viburnum #28 Mine in Iron County (2004). These mines used the Magmont Mill and Viburnum Central Mill near Viburnum #28 Mine, respectively. The Magmont Mill was closed in 1994 and the Viburnum Central Mill was closed in 2000.

There were two smelters constructed in 1967 to handle VT ores. The Buick smelter located in Bixby, Missouri in Iron County processed ore until 1991 and is now used for secondary lead recycling (Seeger, 2008). The Glover smelter closed in 2002 and is located 36 km to the east of the VT in the town of Glover, Missouri about 12 km north of Annapolis, Missouri in Iron County. In 2013, the facility began to be prepared and fitted for new industrial uses.

METHODS

Site Selection and Field Sampling Methods

Available information on previous sediment-Pb assessments, mining source locations, and watershed characteristics for the VT was used to plan the selection of sediment, channel, and floodplain sampling sites used in this study. Published studies and management documents were used to locate potentially contaminated reaches for sampling including: (i) locations of mine and mill outfalls (Seeger, 2008); (ii) prior metal-sediment studies (Femmer, 2004 & 2008; Brumbaugh et al., 2007; Lee, 2008; Hannon, 2012); (iii) Missouri's 2012 303(d) list for impaired streams (http://www.dnr.mo.gov/env/wpp/waterquality/303d.htm); (iv) TMDL documentation (http://www.dnr.mo.gov/env/wpp/tmdl/info/1946-indian-ck-info.pdf); and (v) preassessment screens and determination reports (USF&WS, 2008; USF&WS/MDNR, 2009). Karst influence on the hydrology of ephemeral headwater segments was also evaluated in

Logan Creek and other VT streams during sampling site selection to better understand the relationship between stream hydrology and geomorphic characteristics of bed and bar deposits (Kleeschulte 2008a). The above information was used to determine the study area within which to select stream sites for channel and sediment sampling (Figures 1 & 2). At least 153 km of stream length in the VT were evaluated for sediment Pb contamination during this study (Figure 2 & Appendix C).

Three field assessment procedures were implemented to obtain precise data on channel and floodplain, sediment, and metals characteristics within streams expected to be affected by mining influence. These are: (i) geomorphic survey of in-channel sediment storage; (ii) channel sediment sampling of bed, bar, bench deposits; and (iii) floodplain surveys and soil pit sampling. Photographs of selected sampling sites and sediment features are included in Appendix A.

Geomorphic channel assessment. Field data on channel morphology and in-channel sediment storage were collected at 58 sites within contaminated segments in the Black River, Huzzah Creek, and Courtois Creek drainage basins in June 2012. In addition, five sites on Big Creek and one site on Scoggins Branch were sampled near the Glover Smelter over two visits in April 2012 and February 2013. Sample site density was relatively high for all streams except Crooked Creek where private property and lack of road crossings limited access. Overall, channel site spacing was approximately one sampling site per 1.4 km of the total stream length with the study area. However, sampling intervals were often <1 km in stream segments below mining sites.

Geomorphic measurements were collected from seven transects spaced out at 2 times the active channel width at each sampling site. The active channel is defined by the contemporary stream course and includes both bed and bar/bench deposits between two opposite banks. The channel bed is typically submerged all the time in perennial streams, while bar and bench features may be exposed during low flows, but inundated to varying depths by seasonal high flows or flood events. The middle transect (#4) was located within a glide-riffle transition area within the channel and three transects were added up- and down-stream accordingly. A wooden stake was used as a monument to mark the location of transect 4 and flagging was used to mark each transect. This layout plan produces a sample length of the channel that is about 12 active channel widths long and equivalent to one full meander wavelength of the thalweg, on average (Rosgen, 1996 & 2006). Each sampling reach is located by river-kilometer on the MSU base-map according to the location of the middle transect.

Field measurements using a tape measure, hand level, surveying rod, and tile probe were used to quantify the width and height (or thickness) of individual channel deposits within the active channel along each transect (see examples of field data forms in Appendix B). The width of the total channel was measured using a tight 100 m tapeline. The width of each storage feature was measured individually between landform edge breaks or steep scarp edges. The height of each deposit was measured as the vertical distance from the deepest point in the nearby

channel to the elevation of the top surface tread of the landform (Koehler et al., 2007). The water depth over the channel bed was measured at five to seven equally-spaced points to determine the average bed depth between toe breaks at the base of the adjacent bank or bar. Maximum channel depth was measured using a tile probe in local scour pools to determine the lowest elevation of alluvial storage in the channel. Refusal depths in the channel can indicate the thickness of mobile sediment, flood scour depth, and/or depth to bedrock in the channel (Koehler et al., 2007; Pavlowsky et al., 2010a). The thickness of fine-grained sediment on bench and bank features was also measured with tape or stadia rod at cut-bank exposures or tile probe refusal depths. Duplicate geomorphic assessments were completed for 10 sample reaches located among Indian, Crooked, Neals, Strother, Sweetwater, and Logan Creeks. Relative percent difference values for duplicate measurements of total channel sediment storage by different teams had a median value of 8.5% with a lower quartile of 2.6% and upper quartile of 40.2%.

Channel Sediment Sampling. All channel sediment and floodplain soil samples collected for this study were handled in a similar manner during April 2012 and June 2012. Bed, bar, and bench sediment samples were collected and bagged for laboratory analysis in order to determine textural and geochemical properties (Figures 3 & 4). It is difficult to collect Global Positioning System (GPS) coordinates in a consistent and accurate manner in the VT due to satellite signal interference by high-relief terrain and riparian forest cover. Thus, each sample location is designated by river-kilometer and approximate latitude/longitude coordinates determined by manually locating sites on aerial photographs. Sediment samples collected within a sample reach are considered as representative of the average condition for the reach and therefore are assumed to indicate the character of the central site location. At the large sample masses collected for this study (>0.5 kg), detectable metal contamination of the sample from shovel surface wear or abrasion is improbable. However, only sediment that was not is contact with the shovel surface was collected by hand and placed in sampling bags. In total, 127 sites were sampled for channel sediment for this study (Figure 2 & Appendix C).

1. Bed sediment samples were collected in glide or aggraded plane bed channel units within the active bed of stream (Appendix A-Pictures 3 & 5). Glide sampling occurred in channel areas located at a distance of one or two channel widths upstream of riffle crests which often included pool tail deposits. Aggraded bed sampling occurred where excessive bar deposition occurred such as in disturbance zones or where bar sediment was migrating into and filling the upstream head or middle areas of pools. Both of these channel units are typically inundated by low flows and located within the wetted width boundary of the channel (Figures 3 & 4). A shovel was used to collect a grab sample of bed sediment to a depth of 15 to 20 centimeters (cm). Sampling occurred at bed locations where materials were usually <32 mm in diameter. In some places, surface armoring occurred with a layer of relatively coarse and thin (<10 cm) bed material. Typically, shovel sampling could work through the layer to deeper and finer deposits. However, sampling was avoided in areas where the bed was too coarse (>64 mm) or armor too

thick to penetrate. Up to three channel samples were collected within each sample reach along different transects, if possible. Sometimes the collection of bed samples was limited by water depth, coarse texture of the deposit, and lack of sediment due to exposed bedrock (Appendix A-Pictures 5, 7, 8, 9b, 10a, & 15). Bed samples were typically collected in the center of the channel unit, dewatered by gravity while on the shovel blade, and placed in a 1-gallon plastic freezer bag. Targeted sampling in relatively low velocity and/or shallow areas of the channel and slow removal reduced the rates of fines winnowing from between the coarser bed sediment substrates. During bed sampling, fine sediments surrounding larger clasts were often observed with sedimentary and colored layers still intact in glide units. Pool and riffle sediment sampling was avoided since these areas contained little fine sediment in accessible locations. The amount of fine (<2 mm) surface sediment in pool or riffle units was relatively small compared to the larger volume of sediment in storage within the river channel including buried bed areas and bars which was the subject of the present study. In total, 73 bed sediment samples were collected and analyzed for this study (Appendix F-4). Total sample mass for all bed samples collected ranged as follows: minimum, 198 g; R25, 810 g, median, 1,074 g; R75, 1,354 g, and maximum, 3,801 g.

- 2. Bar sediment samples were collected by shovel at a depth of 3x the maximum pebble size observed on the bar surface in the immediate vicinity to exclude the influence of surface armoring on sample composition and textural measurements (Figure 4). Bars are identified as gravel and sand features deposited along the side or center of the channel with top surface elevations at 25 to 50 percent the channel bank height above the bed (Appendix A-Pictures 3, 4, 11, 12, & 16). Bars can be vegetated or bare. However, fine-grained sediment deposition may occur where vegetation growth slows flow velocities near topographic depressions or higher elevation bar surfaces. If fine-grained sediment layers become thicker than 5 cm on bar surfaces, then the bars were classified as benches for the purpose of this study (see bench description below). Typically 1 to 3 bar samples were collected at each site from one or more transect lines at the approximate center of the bar. The longitudinal location of the sample along the bar feature was recorded as either the head (upstream third of bar length), middle (middle third), or tail (downstream third). Split sample analysis provided good agreement between MSU and USGS methods. Fine-grained sediment percentages determined for samples collected by MSU were similar to a concurrent channel sediment study by the USGS as described in a data report later in the text (e.g., Smith and Barr, 2015). Samples are stored in 1quart plastic freezer bags. In total, 154 bar sediment samples were collected and analyzed for this study (Appendix F-4). Total sample mass for all bar samples collected ranged as follows: minimum, 135 g; R25, 718 g, median, 981 g; R75, 1,416 g, and maximum, 5,000 g.
- 3. Bench deposit samples were collected by shovel to a depth of 10 to 30 cm. Benches are typically identified as relatively narrow surfaces occurring above the elevation of gravel bars, but below the bank-full stage with top surface elevations at 50 to 75 percent the bank-full stage height above the bed (Figures 2 & 3; Appendix A-Picture 2). They can be vegetated or bare. For

the purposes of this study, a bench is characterized by a layer of fine-grained sediment deposited on the surface to a depth of at least 5 cm as determined by tile probe or visually, if obvious. Benches indicate a change in deposition within the channel from lighter-colored gravel or coarse sand such as found on bar surfaces to darker materials containing more silt, clay, and organic matter. Further, vegetation associations may be different on benches compared to nearby bar deposits or floodplain areas. In total, 89 fine-grained bench-top sediment samples were collected and analyzed for this study (Appendix F-5). Total sample mass for all bench samples collected ranged as follows: minimum, 94 g; R25, 179 g, median, 265 g; R75, 490 g, and maximum, 1,903 g.

In addition to the sampling of the sediment deposits described above, nine mud-drape and three mill tailings deposits were also collected for evaluation (Appendix C-2). <u>Mud-drapes</u> form by the deposition of suspended sediment and organic matter in ponded depressions or low flow velocity areas on bar surfaces during the falling stages of higher flows (Appendix A-Picture 4). These deposits selectively trap fine grained sediment in areas more prone to coarse-grained bar transport. <u>Tailings</u> materials were sampled from small drainage channels within the Old Viburnum Tailings Pond.

Additional Logan Creek Sampling by the Missouri Division of Natural Resources (MDNR). Beyond the sediment samples collected by Missouri State University, 31 additional channel samples were collected by MDNR on June 9, 2015 using similar sampling, preparation, and analytical methods. Bed (n=8), bar (15), and bench (8) samples were collected at nine sites along 8 km of Logan Creek from R-km 66.5 to 58.5 including both Adair Creek and Sweetwater Creek confluences. These samples improved the spatial resolution and detection of contaminated sediment in Logan Creek.

Floodplain Assessment Surveys. Floodplain soil investigations were completed at 39 sites during October 2012. In addition, two floodplain sites were surveyed along Big Creek and one on Scoggins Branch in April 2012 and February 2013. Floodplain sites were selected based on knowledge of site access and geomorphic characteristics gained from previous channel and sediment assessments. For the most part, floodplain sampling sites overlapped geomorphic storage assessment sites, but not always. Non-overlapping sites were selected to cover representative floodplain locations where soil survey maps and experience of the investigators indicated better potential for sediment storage and sampling access. Sample site intervals for floodplain coring sites averaged about one sampling site every 3 km stream length.

Information on the topography and thickness of floodplain units was needed to determine the depth and volume of contaminated sediment. In addition, channel dimensions were needed to check that the discharge capacity and floodplain heights were similar to the expected bank-full flood stage (Rosgen, 1996). In contrast to channel storage sampling which collected and averaged geomorphic information from seven different transects at a site, floodplain storage

sampling occurred by collecting one or more cores along a single transect at a site. Further, all core locations were marked by GPS receiver with latitude/longitude coordinates in the field at the time of sampling.

Floodplain-channel cross-sections were surveyed using an auto-level, 100 m tape with pins, and stadia rod that included the channel and bank features, floodplains, and low terrace landforms when possible (Harrelson et al., 1994) (Figure 5; Appendix B). Each Topographic survey transect was geo-located using at least three GPS control points. Horizontal transect distances were measured using a tight tapeline or stadia readings (Rosgen, 1996). Rebar pins or wooden stakes were set at the end of each transect and located with GPS coordinates to allow for relatively precise repeat surveys, if needed. Typically, a team of three persons could complete two to four sites per day.

Field data from channel surveys were used to determine channel dimensions, size of channel bedforms, bank or floodplain heights, channel hydraulic parameters, and minimum/maximum depths of potential mining sediment (Ward and Trimble, 2004; Rosgen, 2006). Geomorphic relationships between channel discharge capacity and the top bank height for terrace, floodplain, and bench features were evaluated for a subset of VT sites to verify bank-full channel elevations (Figure 6). Discharge was calculated using Manning's equation in HydraFlow Express software for stages corresponding to the height at which water begins to inundate the top surface of each landform along the survey. The Manning's equation is a standard method in hydrology where flow velocity is estimated for any channel stage where direct flow measurements are not available using three variables: channel slope, hydraulic radius (which is similar to mean depth), and roughness coefficient often referred to as "Manning's n" (Rosgen, 1996; Ward and Trimble, 2004). A typical n value of 0.04 for Ozarks streams was used in the hydraulic analyses for this study (Pavlowsky and Martin, 2010). Channel flow capacities at several stages were compared to rural regression flood frequency relationships that use drainage area and other basin characteristics to estimate peak flood discharges for a range of flood frequencies from the 2 to 500 year recurrence interval (RI) (Alexander and Wilson, 1995). Valley floor landforms sampled for this project were all inundated by floods <5-yr RI and typically <2-yr RI which suggests that flood-related sediment deposition has occurred throughout the mining period (Figure 6). As expected, bank-full stages for floodplain along VT stream channels indicated flood frequencies of approximately 1.5-yr RI (Rosgen, 1996; Simon et al., 2004).

Floodplain Sediment Sampling. In contrast to benches, floodplains are defined by wider surfaces at higher elevations located on valley floor areas adjacent to the channel, but not within it, to exclude bench surfaces (Figures 3 & 7). Overbank floodplains typically contain fine-grained material, but can contain massive or bedded sand and gravel deposits due to transport by extreme flood events and coarser sediment loads, episodes of local aggradation, and overbank splay deposition (Appendix A-Pictures 1 & 10b). Floodplain deposits may have been

contaminated by fine-grained sediment transported during floods as suspended load or aerial deposited particulates from past smelter operations or wind-blown tailings.

Floodplain soils were sampled at intervals of 5 to 10 cm from the walls of 0.5 m deep pits dug with a shovel or trowel (Figure 7). Sometimes floodplain samples were collected, in a similar manner as pits, from cut-bank exposures where the stratigraphy was clearly shown and no slumping is indicated. In general, floodplains were not expected to be contaminated below 0.5 m since mining contaminants began to be released relatively recently (since 1960) and contemporary overbank sedimentation rates in rural watersheds similar to the VT tend to be <1 cm/yr (Owens et al, 1999; Lecce and Pavlowsky, 2001; Owen et al., 2011). Further, the vertical extent of fine-grained overbank floodplain sampling was usually limited by refusal on coarse channel bar deposits buried at depths <50 cm. Field notes on the stratigraphy (color, texture, structure, artifacts) of the exposed soil profile were collected at each core site (after Schoeneberger et al., 2002). As expected, the floodplain profiles sampled lacked weathering features and sub-surface soil horizon development suggesting recent deposition. A folding ruler was used to maintain depth control during sampling with a small trowel. Samples were collected and immediately placed in labeled 1-quart plastic freezer bags for transport. Overall, floodplain soil sampling occurred at 38 sites from 112 individual pits sites (including cut-bank sampling) to various depths generating 498 individual floodplain soil samples for the study. Total sample mass for all floodplain samples collected ranged as follows: minimum, 88 g; R25, 169 g, median, 213 g; R75, 301 g, and maximum, 1,636 g.

Laboratory Methods

Laboratory methods involve the preparation, physical analysis, and geochemical analysis of sediment and soil samples. For the most part, all laboratory work to analyze sediment samples collected by MSU was carried out by the Ozarks Environmental and Water Resources Institute at MSU (http://oewri.missouristate.edu/). However, the results of two other studies were used to evaluate contamination trends in the present study. Split samples from ten bar sediment samples collected by MSU were analyzed by the U.S. Geological Survey (USGS) at Rolla, Missouri (Smith and Barr, 2015). In addition, 31 channel sediment samples were collected by the Missouri Department of Natural Resources (MDNR) on June 9, 2015 using sampling and XRF methods similar to the present study (Appendix I). A mine waste spill occurred on Adair Creek after the sampling phase of the present study was completed. Therefore, MDNR decided to collect samples from Logan Creek to evaluate recent changes in sediment metal levels.

<u>Sample Preparation.</u> All sediment samples were stored in labeled resealable plastic bags in the field with sample number, location, and field description verified according to field notes upon receipt by the laboratory. After delivery to the laboratory, all sediment samples were dried in a 60°C oven, ground with mortar and pestle, and passed through a 32 mm sieve, if needed, to

remove large sediment particles and then a 2 mm sieve prior to the first round of Portable X-Ray Fluorescence spectrometry (XRF) analyses.

<u>Sediment Texture.</u> Manual sieving methods were used to separate the bulk sediment sample into three fractions: (1) fine gravel, <32 mm to >2 mm; (2) coarse and medium sand, <2 mm to >0.25 mm; and (3) fine sand, silt, and clay, <0.25 mm. As used in this study, "bulk sample" refers to only that portion of the sampled material <32 mm in diameter. For most samples, there were no particles larger than a sieve size of 32 mm. However, in some samples, larger materials were collected and removed during the sample preparation phase.

<u>Geochemical Analysis.</u> The geochemistry of the <2 mm sediment fraction was used to determine the contamination level of the sediment, indicate the influence of mining source inputs on sediment composition, and evaluate the chemical conditions prevalent within the deposit. In addition, metals analysis of the <250 um fraction was also evaluated to better understand the size distribution of Pb in channel deposits. The following geochemical data were collected for this study:

- 1. Total and inorganic carbon analysis. A Carbon/Nitrogen/Sulfur (CNS) analyzer was used to determine the carbon content and to distinguish between organic matter and mineral grains in the <250 um fraction for 73 bed samples and 142 bar samples. "Total carbon" is determined on an untreated sample and "inorganic carbon" is determined after burning off the organic carbon as CO₂ in a muffle furnace at 400° Celsius. Since the primary host rock of the mineralization in the VT is dolomite, it is anticipated that tailings particles within alluvial sediment will have higher inorganic carbon content in the form of carbonate (Ca-Mg CO₃) compared to background sediment where weathering and leaching over time has removed the carbonate and lowered the inorganic C concentration. Further, "organic carbon" is determined as the difference between total and inorganic carbon fractions. The presence of high levels of organic carbon in a sample may indicate a higher sorption capacity for dissolved metals to bind higher concentrations of Pb from mining sources. The standard operating procedure for the method used in this study can be found at http://oewri.missouristate.edu/58411.htm.
- 2. Elemental and metal analysis. Levels of lead, zinc, copper, cobalt, and nickel found in the samples indicate the level of mining pollution in relation to contamination thresholds. Mining-related metals concentrations in the <2 mm and < 250 um sediment size fractions were used to quantify the contribution of mining metal inputs to sediment geochemistry at a given location in the stream network. X-ray fluorescence spectrometry was used in the laboratory to analyze the geochemistry including Pb concentrations in all sediment samples evaluated for this study (USEPA, 1998). An **Oxford X-MET3000TXS** portable XRF analyzer was used and specifically calibrated for determining the geochemistry of soil. The instrument detection limits reported by the manufacturer for metals evaluated in this report are as follows: 18 ppm Co, 15 ppm Cu, 15 ppm Pb, 16 ppm Ni, and 8 ppm Zn (OEWRI, 2007). Detection limits for metals not reported

by the manufacturer were determined independently as 400 ppm Ca, 100 ppm Mn, and <1,900 ppm Fe (Pavlowsky et al., 2011). The minimum acceptable accuracy and precision is 20% with duplicate errors (95% CL) typically <10% (OEWRI, 2007; Pavlowsky et al., 2011). The standard operating procedure for the XRF analysis method used in this study can be found at http://oewri.missouristate.edu/58411.htm.

3. Cesium-137 radioisotope analysis. Cesium-137 profiles are used to date sediment layers in floodplain cores by correlating peaks in activity to specific years of documented atmospheric fallout of Cs-137 (Walling and He, 1993; Owens et al., 1999) (Figure 6). Radioactive Cs-137 is formed when uranium and plutonium absorb neutrons and undergo fission in nuclear reactors and during detonation of nuclear weapons (Lelieveld et al., 2012). Nuclear bomb testing began to release significant Cs-137 levels to the atmosphere in 1952 with measureable activities in soil in 1954. In the northern hemisphere, major peaks in global deposition occurred in 1958 and 1963-64 and minor peaks in 1971 and 1974 (Ritchie and McHenry, 1990). In addition, nuclear plant accidents such as at Chernobyl in April 26, 1986 may also enrich sediment layers with Cs-137 (Lima et al., 2005; Belyaev et al., 2013). Since there are no natural sources of Cs-137 and its half-life is 30 years, Cs-137 profiles provide a precise temporal record to identify floodplain soil deposited during the mining period in the VT. In undisturbed floodplain soil locations with relatively uniform sedimentation rates, the maximum Cs-137 peak in 1963-64 should coincide with the beginning of mining and stream sediment contamination in the VT between 1962 and 1966 (Femmer, 2008). To measure the activity of Cs-137, about 50 grams of dry <2 mm soil material is put in an Marinelli beaker and analyzed for 24 hours using a GC4020 GE Co-Axial Detector and DSA 1000 Digital Spectrum Analyzer with 747 Series Lead Shield to identify and quantify gamma-ray emitting radionuclides. The standard operating procedure for the method used in this study can be found at http://oewri.missouristate.edu/58411.htm.

Calibration and Correction of MSU-XRF Data

Duplicate bar sediment analysis by MSU and USGS. Ten bar sediment samples were collected from VT streams by MSU in February 2013 (Appendix D). Individual bar samples were mixed in a plastic bucket by hand and split in the field with one set analyzed for texture and geochemistry by MSU and the other by the USGS in Rolla, Missouri. The comparison of the results between both laboratories provides a quality control check for the present study. Particle size distributions determined by both USGS and MSU were similar and had similar levels of precision typically within +/- 15% relative standard deviation (RSD). MSU only used XRF analysis for geochemical analysis. However, the USGS used two techniques to quantify sediment geochemistry for the duplicate samples. Similar to MSU, the USGS used a portable XRF analyzer instrument (Thermo Fisher Scientific, Waltham, MA) to measure metal concentration in bar duplicates. In comparison, MSU XRF precision estimates were similar to those from USGS XRF analysis at +/- 10-20% RSD (n=3) or percent difference (RPD) (n=2). If a normal distribution is assumed, then these two error terms are directly linked as: RSD x 1.414 = RPD. However, MSU-

XRF results for Pb trended higher compared to the XRF results reported by the USGS. In addition, duplicate samples were also analyzed by the USGS using four-acid total digestion with inductively coupled plasma atomic emission spectrometry (ICP-AES) at the USGS national laboratory in Denver, Colorado. Again, the precision for MSU XRF and USGS ICP results was similar and in the same range. However, MSU-XRF Pb concentrations were linearly related, but slightly higher, than the geochemical results of the USGS ICP analyses (Appendix D). Regression equations correlating raw MSU-XRF values to paired USGS-ICP values for all metals and size fractions evaluated in this study with concentrations in ppm are listed below:

<2 mm Fraction	
Pb ICP = 19.1 + 0.660 x Pb-raw	$r^2 = 0.99$
Zn ICP = 22.3 + 0.699 x Zn-raw	$r^2 = 0.99$
Cu ICP = 0.58 + 1.374 x Cu-raw	r ² =0.99
Ni ICP = -8.5 + 1.401 x Ni-raw	$r^2 = 0.93$
Co ICP = -14.3 + 0.823 x Co-raw	$r^2 = 0.79$
<250 um Fraction	
Pb ICP = -26.5 + 0.741 x Pb-raw	$r^2 = 0.99$
Zn ICP = -57.3 + 0.750 x Zn-raw	$r^2 = 0.99$
Cu ICP = 10.1 + 1.341 x Cu-raw	$r^2 = 0.99$
Ni ICP = 12.1 + 0.668 x Ni-raw	$r^2 = 0.71$
Co ICP = -20.6 + 0.699 x Co-raw	$r^2 = 0.96$

Analytical results for XRF can vary from those of other methods due to the differences in technique for element detection, strength of acid treatments, and mineralogy and elemental distribution of sediment samples (Arbogast et al., 1987). For example, the mean Pb concentration using MSU's portable XRF for 10 analyses of USGS geochemical reference standard GXR-1 was 856 ppm Pb. In comparison, mean Pb concentrations determined for the same reference standard by nine different laboratories with varying methods ranged from 604 to 979 ppm Pb (Arbogast et al., 1987).

Previous quality control testing by MSU using the same XRF analyzer confirmed a detection limit of 15 ppm Pb with a threshold at 32 ppm below which detection and replicate errors increase (Pavlowsky et al., 2011). Lead concentrations measured in Ozark river sediment samples using XRF analysis were usually within +/- 15% those determined by ICP-AES analysis of aqua regia extracts (treatment with hot concentrated nitric and hydrochloric acids). These tests included samples from uncontaminated and contaminated river floodplain soils affected by mining contamination (Pavlowsky et al., 2011).

<u>Correction of MSU-XRF results to USGS-ICP equivalent values.</u> The toxicity threshold values for metals used in this study were originally derived by analysis of the un-sieved, fine-grained

sediment fraction using strong acid digestion and ICP-AES to determine total metal concentrations (MacDonald et al., 2000). In order to properly apply the threshold values to the sediment metal analyses in the present report, MSU-XRF results were converted into USGS-ICP equivalent values for contamination determinations and storage calculations using average values of ratios between USGS-ICP and MSU-XRF results (Table 2; Appendix D). Samples with below detection results were omitted from ratio analysis. Out of the ten total duplicate split samples evaluated, there was one below-detection analyses for the <2 mm fraction (Site 5-West Fork). To check for the effect of the one missing ratio value on the mean Pb ratio value used to correct MSU-XRF results, the missing value was estimated by using a regression equation to predict the <2 mm Pb concentration from the <250 um Pb concentration for each sample (r2=0.95). The recalculated mean ratio based on the estimated Pb value did not change to a significant degree (only +1%). Therefore, it was assumed that the Pb ratio used for correction purposes was robust, albeit based on only 9 of 10 samples. Metal concentrations converted into USGS-ICP equivalent concentrations using the ratio method are referred to as "corrected" XRF data in this report. Corrected XRF values for the <2 mm fractions were used to evaluate contamination and metal toxicity in VT stream sediments (Table 3). The mean ratio values for each of the metals evaluated that was used to correct raw MSU-XRF results for the <2 mm fraction of channel and bench sediment samples in order of increasing RSD value in parentheses are as follows: Cu, 1.40 (5%); Ni, 1.20 (12%); Pb, 0.72 (16%); Fe, 1.11 (21%); Zn, 0.86 (25%); Mn, 0.70 (33%); Co, 0.61 (36%); and Ca, 0.40 (68%) (Table 2). RSD values less than 30% are generally acceptable for environmental sediment studies (Smith and Barr, 2015).

Geospatial Data and Analysis

A geospatial data base and Geographic Information System (GIS) analysis was used to organize and analyze all the field and laboratory data evaluated in this study. High resolution 2007 aerial photographs were used as a base map for this study. The aerial photograph data was USGS 2 ft resolution leaf-off digital orthophotography acquired 3-8-07 to 4-7-07 and downloaded from MSDIS (msdis.missouri.edu). Geospatial technologies and analysis are used in this study to assess sample reach characteristics, determine watershed and channel variables, and calculate the volume of contaminated sediment storage.

Sample Reach Location and Mapping. Latitude and longitude coordinates collected from GPS receivers or aerial photograph points were stored in a GIS and displayed on the 2007 base map. MSU developed a river-kilometer system for the entire VT and Big Creek stream network to use as a spatial reference for site location during field sampling and quantitative analysis of sediment data (Figure 2). High-resolution GPS or available Digital Elevation Models (DEMs) were used to determine an elevation for each channel survey.

<u>Channel Planform Mapping.</u> This study found a strong relationship between planform width and sediment storage in VT streams and used this relationship to predict storage volumes for all

contaminated segments. Field measurements of active channel width and sectional areas of stream deposits were used to develop regression equations between active channel width (m) and channel sediment storage (m³ per m channel length). These equations were used to predict sediment storage for un-assessed channel reaches using active channel width values generated from analysis of 2007 aerial photographs by river-kilometer at 300 m intervals. The active channel width includes the entire width of the channel from bank to bank including all bed, bar, and bench units (Figure 7). Channel planform delineation and mapping uses the same methods as reported in Martin and Pavlowsky (2011) and Owen et al. (2011).

Contaminated Floodplain Mapping. All the counties covering the Viburnum Trend have published soil surveys available along with GIS data layers of the soil series maps and soil attributes. The soil surveys for each county are: Brown and Greeg (1991), Iron Co.; Larson and Cook (2002), Crawford Co.; Simmons and Childress (2005), Shannon Co.; Simmons et al. (2006), Reynolds Co.; and Skaer and Cook (2005), Washington Co. These soil maps were used to help plan field work and identify flood-prone soils and floodplain units on the valley floors of VT streams. Published soil descriptions from soil survey reports and field evaluations by MSU were used to interpret the elevation and age of floodplain units that were expected to contain contaminated mining sediment. It was expected that contaminated floodplain soils would be associated with mapped soil series on relatively low elevation valley positions, exposed to frequent flooding, and having relatively young and poorly-developed profiles with A/C or A/Bw horizons. Field sampling and assessment of metal contaminant profiles are used to verify floodplain interpretations.

Sediment Storage Variables and Calculations

Contaminated Sediment Storage in the Active Channel. The volume of contaminated inchannel sediment storage was calculated for each sample reach based on field measurements of width, height or depth of different channel deposits. In-channel sediment storage was assessed at each transect and averaged across the seven sampling transects to determine the mean channel sediment storage for the site in units of m³ of sediment per meter channel length by multiplying deposit width (m) x deposit thickness (m) to determine cross-sectional storage area (m²). Storage area was then multiplied by a unit channel length (1 m) to report average site storage in m³/m. Six in-channel storage components were quantified for analysis including bed, bar, coarse-grained bench, bench-top, total storage, and bar storage above the water line (Figure 3 & 4):

1. Bed storage includes the sediment stored within the channel bed between bank or bar toe locations and from the bed surface to the lower boundary of unconsolidated material below the bed as indicated by deepest probe or scour pool depth. In general, it was assumed that this deepest bed elevation was a good approximation of the vertical limit of alluvial sediment storage within a stream valley (Koehler et al., 2007). During flood events, bed materials are

mobilized and turbulent flows can scour and erode to bedrock along the channel bed. Over periods of years to decades, the deepest thread of the channel referred to as thalweg, migrates back and forth across the entire width of the active channel and forms a relatively horizontal platform with relatively uniform depth underlain by bedrock or coarser lag deposits. The formation of the channel platform is related to the degree of erosion caused by floods and the resistance of sedimentary materials or bedrock to erosion. Channel bed and bar sediment may be deposited on the platform during flood recession or where the thalweg has shifted away.

The material deposited within the present channel bed is typically below the water table and so is expected to trap fine-grained sediment in pore spaces during low flow periods. Further, these fine sediment deposits can sorb dissolved metals from the overlying water column and infiltrating stream flows. Thus, aquatic life in bed sediment substrates can become exposed to fine-grained sediment and associated metal contaminants even though the bed is affected by higher flow velocities that tend to maintain a relatively coarse surface. Fine sediment embeddedness is an important indicator of aquatic habitat quality in Ozark streams that describes the degree to which fine sediments are incorporated within coarser bed deposits such as riffles (Panfil and Jacobson, 2001; Sarver, 2003).

2. Bar storage includes the gravelly sediment within channel bars and benches located adjacent to and below the top elevation of the channel bed. Lower elevation channel deposits such as low relief bar deposits tend to be relatively coarse with fines embedded within pore spaces. Bar and bench sediment in general provide an indicator of annual to decadal periods of storage of sediment and associated metals within the channel. Due to sampling depth limitations, buried bar deposits at depths >0.4 m were rarely sampled and their characteristics were assumed to be similar to samples of bed and upper surface bar materials collected from the same reach. Results of bar coring studies by the USGS suggest that this assumption is acceptable since grain size and Pb contamination trends tend to be similar for upper surface and more deeply buried bar units to the depths of bar and bed deposits measured by MSU and used in sediment storage calculations for this study (Tables 18 & 19) (Smith and Barr, 2015).

In this study, bar deposits are active features subject to recent deposition or reworking, lacking or having little vegetation cover, and composed mainly of sand and gravel with some cobble-sized materials. Bars can be covered in places by a thin layer of fine sediment <5 cm. As elevation of the bar surface increases above the bed, the size of sediment tends to decrease and it is possible for sand and mud layers to be found on the highest bar surfaces especially where vegetation or other obstacles such as large woody debris, bedrock blocks, or artificial structures reduce flow velocity. Sediment deposits on bar surfaces located at higher elevations and/or exposed to direct currents during higher flows are expected to be more available for entrainment and reworked more often by channel flows compared to bar units buried at depth or located in protected areas. Further, the most recent deposits tend to form on the upper and

laterally accreting surface of actively-forming bars, particularly at the tail end of the bar or at point bar locations opposite eroding cut-banks.

- 3. Coarse-bench storage includes older bar deposits that are now relatively stable with vegetation cover and fine-grained sedimentation on upper surfaces. Bench surface elevations are often slightly higher than adjacent bars. Coarse bench deposits are similar to bar deposits in origin and overall texture, but are covered by fine-grained sediment deposits thicker than 5 cm with moderately dense vegetation growth.
- 4. *Bench-top storage* includes the fine-grained sediment deposited uniformly across a bar surface to a thickness of 5 cm or more. Typically, bench surfaces will be vegetated to some degree with grasses or forbs, willow and sycamore saplings, or a young riparian forest. Bed and bar units are typically composed of coarser gravel deposits with <30% sediment finer than 2 mm in particle size (i.e., total sand, silt, and clay). In contrast, bench storage units are typically composed of >80% of material <2 mm in size. Thus, since bench sediments tend to be finergrained overall, they have the geochemical capacity to sorb metals to higher concentrations and contain relatively high masses of metals per unit volume compared to the coarser bed and bar units (Miller and Orbock-Miller, 2007).
- 5. Total channel storage includes the total volume of sediment stored within the sample reach as the sum of units from 1 to 4 above. Total storage is calculated as the sum of two components: (1) coarse sediment storages including bed, bar, and lower bench deposits; and (2) fine-grained bench-top deposits. Coarse sediment storages are assumed to be composed of similar materials and so the same sediment and geochemical properties are applied each for a given site. Bench-top units can differ in texture and metal content compared to coarse deposits since they form in lower energy environments at higher elevations in the channel where fine-grained sediments tend to deposit during higher flows.
- 6. Bar storage above the low flow waterline includes the portion of a bar deposit that is above the low-flow water line in the channel as measured at the time of sampling. The volume of active bar sediment above the waterline is an indicator of the amount of sediment available for excavation if it is contaminated with Pb above 128 ppm. Bed deposits provide habitat for aquatic life and so are not the preferred target for disturbance by excavation practices unless a severe toxic threat exists. Benches are covered by soil and vegetation and therefore support more diverse ecological services compared to active bars.

<u>Channel Width-Storage Relationship.</u> In this study, a strong, positive relationship was found between average active channel width of the stream reach and cross-sectional sediment storage (r^2 = 0.91 for total storage over active width). Therefore, regression equations describing the active channel width to sediment storage volume relationship were used to predict storage volumes for un-measured channel sites. Average active channel width values

were determined at 300 m intervals from high resolution 2007 aerial photographs for the mining-contaminated segments. This process produced a high resolution data set for active channel width of VT streams which was used to calculate total and fractional storage components for all contaminated segments using empirical regression equations. To determine the total storage for a given contaminated segment, the series of aerial photograph widths at 300 m intervals were corrected to field width using a regression equation that predicts field width from aerial width (Appendix G-4). Regression analysis revealed a strong correlation between width measurements from aerial photographs and field-based width measurements among individual storage assessment sites (r²=0.76). This strong relationship further validated the accuracy of using aerial photograph width from 2007 as representative of actual channel width in 2012. Therefore, aerial photograph widths from 2007 were used to predict corrected-2012 widths for all contaminated channel segments including sites where field measurements were previously collected. Finally, the aerial-to-field corrected-2012 active widths were then used in the regression equation to predict sediment storage for all field sampled and unmeasured sites within contaminated stream segments.

This geomorphic approach to quantifying the spatial distribution of channel sediment storage based on active channel width is valid for three reasons. First, it well established that channel width tends to increase downstream with increasing drainage area (Rosgen, 1996; Panfil and Jacobson, 2001). As a result, the thickness of aggraded sediment, alluvial fill, and bar deposits will also tend to increase in scale with width downstream. Second, wider streams at a given drainage area will tend to contain more bar area and thus store greater volumes of sediment. In Ozark streams wider planforms tend to be associated with disturbance zones or active channel reaches associated with excess sediment storage compared to narrower upstream and downstream reaches (Jacobson 1995). Further, these active reaches of sediment deposition can be effectively measured using aerial photograph analysis (Jacobson and Gran, 1999; Martin and Pavlowsky, 2011). Third, Ozark stream bed elevations are typically close to bedrock and are often confined by shallow bedrock depths along the bed and banks, thus reducing the space and range of variability available for bed sediment storage (Panfil and Jacobson, 2001; Martin and Pavlowsky, 2010). Following, if depth adjustments are limited, then geomorphic channel responses to discharge and sediment regime changes are expected to affect channel width more than depth, thus making width a sensitive indicator of the volume of alluvial storage within a reach.

Contaminated Soil Storage in Floodplains. In a similar manner as with in-channel sediment volume, contaminated floodplain storage (m³) per unit valley length (m) was calculated by multiplying average cross-valley width (m) of the fine-grained overbank floodplain by the average depth (m) of contamination >345 ppm Pb and multiplying by the unit length of the valley (1 m). The 345 ppm threshold was used to identify the depth of contaminated soil in pit profiles. Contaminated floodplain dimensions were based on cross-valley topographic surveys and the analysis of pit samples from transects located at sites below mining sources in

contaminated segments (Figures 3, 5, & 7; Appendix B). A series of pits were sampled along each transect to evaluate Pb contamination for different floodplain surfaces, each with different elevations caused by variations in flood magnitude and sediment transport regime during formation. If the cross-valley survey did not include the entire landform, the width was estimated from soil maps and aerial photographs. The downstream lengths of contaminated floodplain segments were based on locations of permitted mine outfall points, similar valley and channel morphology, locations of major tributary junctions, and sampling interval of transects within a given stream. Contaminated floodplain segments tended to overlay channel segments, but in some cases, floodplain segments were composed of more than one channel segment. Careful examination of floodplain cores was important since different floodplain features within a reach may vary in sedimentation rate, grain-size distribution, organic matter content, contamination level, and other geochemical characteristics (Lecce and Pavlowsky, 2004; Owen, et al., 2011).

Calculation of Lead Metal Storage. The volume of contaminated sediment stored in VT stream systems was defined as the total volume (m³) of the entire bed, bar, bench, or floodplain deposit within which the <2 mm sediment fraction contains >128 ppm Pb for channel sediment and >345 ppm Pb for floodplain soil (Table 3). The composite of all sediment sizes stored within an alluvial deposit was referred to in this study as the bulk sediment volume. While all stored sediment can potentially be remobilized by erosion and be a threat to aquatic life, the total amount of Pb metal in storage that is available for future remobilization is not specifically indicated by total volume since the concentration of Pb varies spatially downstream and among individual storage units at a site. Further, previous studies indicate that relatively low concentrations of mining-related metals are found in sand-sized and larger diameter particles in VT streams (Brumbaugh et al., 2007; Femmer, 2008; Lee, 2008).

To account for variations in sediment deposit texture and variable mining-metal inputs, the mass of Pb metal stored within the contaminated sediment deposit or soil was also determined. In general, the amount of Pb stored in an alluvial deposit of a given volume can vary based on the concentration of Pb and percentage of fine-grained sediment. To calculate the mass of Pb stored in a segment, the volume (m³) of the contaminated alluvial deposit is first multiplied by the bulk density of the material to determine the total mass (Mg) of contaminated sediment or soil in the deposit. Bulk density values used in this study were 1.4 Mg/m³ for floodplain soil and fine-grained bench sediment and 1.8 Mg/m³ for bed and bar sediment. Bulk density of river deposits can vary spatially depending on texture, sorting, and age/compaction (Bunte and Abt, 2001). For example, the bulk density of silty or loamy floodplain soils in the Ozarks can range from 1.3 to 1.6 Mg/m³ (Simmons et al., 2006). In general, sand deposits have bulk density values ranging from 1.6 to 2.0 Mg/m³ (Manger, 1963) and mixed gravel deposits from 1.7 to 2.6 Mg/m³ (Bunte and Abt, 2001). Therefore, given the ranges of bulk density above, bulk density values within similar deposit types can be expected to vary by +/- 20%.

After the mass of the entire "bulk" deposit was calculated, the mass of fine-sediment (<2 mm) within the segment was calculated by multiplying the total sediment mass by the mass fraction of <2 mm-sized particles within the deposit (i.e., mass fraction = <2 mm % / 100). Finally, the fine-grained sediment mass is multiplied by the mass fraction of <2 mm Pb (i.e., mass fraction = Pb concentration (ppm) in the <2 mm sediment fraction / 1,000,000) to determine the mass of lead stored in fine-grained sediment in the segment. To evaluate only mining Pb contributions on the sediment Pb burden, a background concentration of 17 ppm Pb was subtracted from the <2 mm Pb concentrations for bed, bar, and bench deposits prior to mass storage calculations. The background concentration value was determined from the analysis of six uncontaminated channel sediment samples collected by MDNR from Logan Creek upstream of Adair Creek using similar methods as the present study. The threshold background concentration was calculated as the arithmetic mean of the Pb concentrations from the six samples (7 ppm) plus 3-times the standard deviation (3.3 ppm) to yield a background threshold value of 17 ppm Pb. The same XRF unit used for the USGS companion study was also used to analyze the background samples so that the geochemical results were consistent with the corrected MSU XRF values used in this study. Recall, sediment storage volumes were based on geomorphic field assessments of VT stream channels, mass fractions of fine-sediment in the sediment deposit were derived from particle size analysis of field samples in the laboratory, and Pb and other metal concentrations were determined from field samples using corrected XRF analyses of the <2 mm fraction.

<u>Bar Coring Investigations by the USGS</u>. The USGS at Rolla, Missouri collected and analyzed core samples from several channel bar sites in the VT (Smith and Barr, 2015). The present study used the coring data from the USGS study to evaluate if the maximum depth of contamination determined for channel bar deposits using geomorphic field measurements were representative of actual contaminated core depths. Analysis of the <2 mm fractions of the USGS core samples were completed using a Thermo Fisher Scientific XRF (Waltham, MA) than used by the laboratory at MSU. The depth of contamination in the USGS bar cores was evaluated for both the <2 mm and <250 um sediment fractions.

Left-Censored Data Analysis

Geochemical datasets for stream sediments are often left-censored since instrument and procedure limitations result in non-detections at the low end of the concentration range near zero or at the detection limit. The instrument detection limit for Pb reported by the manufacturer of MSU's XRF unit is 15 ppm. In this study, all non-detections for the <2 mm fraction are replaced by 10 ppm values. This value approximates 0.5 to 0.7 times the detection limit which is an acceptable substitution method to support geochemical analysis for this type of dataset often performing as well or better that other statistical methods, such as Kaplan-Meier estimation, according to the Army Corp of Engineers (Clarke, 1998), USGS (Antweiler, 2008; Antweiler and Taylor, 2015), and other government agencies (Leith, et al., 2010). The dataset used for geochemical analysis of sediments in Viburnum Trend streams has several

characteristics which make the simple substitution method effective: (i) relatively low number of left-censored values (<30%); (ii) detection limit is relatively small compared to the high range and maximum values of Pb concentrations in sediment samples (>200 x DL); (iii) focus of analysis is on contaminated samples with greater than 128 ppm Pb and far above the censoring limit; and (iv) quantitative analyses used in the study utilize correlation and ranking of data pairs and not time series or multiple regression analysis that are more affected by censoring errors.

RESULTS AND DISCUSSION

For this study, channel sediment and floodplain soil samples for metals analysis were collected at a total of 127 different sites from VT streams including Big Creek (Figure 2a-f). In total, XRF metals analyses on the <2 mm fraction were completed on 868 sediment and soil samples (Appendix C). Sediment and metals results were evaluated based on location within the drainage network relative to tributaries and mine source points (Appendix E). The <250 um sediment fractions of 73 bed and 142 bar samples were also analyzed for metals and further analyzed for inorganic and organic carbon (Appendix C-3). Corrected XRF Pb values for the <2 mm and <250 um fractions for channel sediments were used to determine the location and length of contaminated segments in the VT (Table 3; Appendix F-4 & 5). The <2 mm fraction was used for the primary determination of contaminated sediment and evaluation of contaminated stream length.

Stream Sediment Contamination by Lead and other Metals

Background concentrations of Pb in VT stream sediments not affected by mining tend to be inversely related to grain-size since finer-grained sediment rich in silt and clay has more surface area and binding capacity compared to larger particles in the sand size range. Background Pb concentrations tend to be <10 ppm for the <2 mm sediment fraction (Brumbaugh et al., 2007), <20 ppm for <250 um fraction (Hannon, 2012), and <50 ppm for the <63 um fraction (Lee, 2008). Brumbaugh et al. (2007) reported a maximum Pb enrichment factor of 95x and Lee (2008) a median enrichment factor of 10x for VT stream sediments from mining areas. While the emphasis was to sample contaminated streams, this study found background Pb levels similar to those reported in previous studies. Lead concentrations below 30 ppm were measured in near-by and similar Ozark tributary and mainstem streams above mining areas and in pre-mining age floodplain soils. Moreover, six channel sediment samples collected in June 2015 by MDNR on Logan Creek above mining influence by Adair Creek had a mean Pb concentration of 7 ppm with a standard deviation of 3.3 ppm in the < 2 mm fraction In contrast, the <250 um sediment fraction had a mean concentration of 15 ppm with a standard deviation of 6.8 ppm Pb (appendix I).

Overall, Pb detection in channel sediments was good with measured Pb occurring in 64% of the bar samples and 77% of the bed samples for both the <2 mm and <250 um sediment fractions (Appendix F-1). There were strong linear relationships between sediment Pb concentrations in the <2 mm and <250 um fractions (Appendix F-2 & 3). In cases where Pb was measured for one size fraction, but was not detected in the other, regression equations were used to predict the non-detected values (Appendix F-4). In general, Pb concentrations in the <250 um fraction of bed and bar sediments were 1.5 to 3 times those in the coarser <2 mm fraction (Appendix F-2 & 3). In cases where Pb was not detected in either fraction, assumed concentrations were applied to the data set as 10 ppm for <2 mm and 30 ppm for <250 um fractions (Appendix F-4 & 5). Given that Pb concentrations in the <250 um fraction were typically three times those in the <2 mm fraction, the substituted values for non-detects at 30 ppm reflected this geochemical trend.

Texture and Pb trends in sediments from VT Streams. Lead was used as the primary indicator to evaluate the level of contamination from mining sources in this study. Therefore, it was important to utilize as large a sample size as possible to determine the extent of contamination in VT streams. To maximize the number of sediment Pb samples for consideration, the dataset containing Pb and grain-size results for bed, bar, and bench deposits was corrected to replace below detection values in two ways (Appendix F-4). First, below detection values in the dataset were given assumed values at 0.7 times the detection limit (i.e., 15 ppm x 0.7 = 10 ppm) using an accepted method of dividing the detection limit by the square root of 2 as previously described in the discussion of left-censored data analysis above. Second, regression equations were used to predict missing values for Pb concentration and texture for one size fraction from a positive result of the other (Appendix F-3). R-squared values for the regression equations used to correct missing values ranged from 0.4 to 0.44 for texture and 0.86 to 0.87 for Pb concentration.

Overall, the percent <2 mm fraction in bulk sediment samples generally increased with elevation above the channel bed, following expected influences of fluvial sorting and flow energy on sediment transport. The %<2 mm fraction averaged 30% for bed sediment, 41% for bar sediment, 72% for floodplain soil, and 78 percent for bench sediment (Table 4). The <250 um fraction typically comprised <10% of bulk bed and bar deposits with median values of 2.3 and 3.8 percent and mean values of 6% and 8%, respectively. The standard deviations of the entire VT sample set were relatively uniform among deposits and ranged between 20 to 25 fraction percent yielding RSD% values of about 65% for bed and bar sediment and 30% for bench and floodplain sediment. The geometric mean of Pb concentrations in the four deposit types increased in the following order: bar sediment, 51 ppm; floodplain soil, 90 ppm; bed sediment, 141 ppm; and bench-top sediment, 144 ppm Pb (Table 4). Geometric RSD% values ranged from 31% to 39% for Pb concentration in sediment.

Average sediment size and Pb concentration values were calculated for individual stream segments to develop a framework upon which to evaluate contamination level and compute sediment storage volumes. As described previously, the stream network was divided operationally into 31 segments based on mine location, stream length, tributary confluences, and sampling site density (e.g., Table 5). Average segment values for texture and Pb concentration were computed for each deposit type in each segment. If a sample of one deposit type was missing from the segment, it was predicted using ratios of the average value of one deposit type to another. For example, if a bar sample was missing in a segment, its % <2 mm value was calculated by multiplying the bed mean value by the bar:bed ratio derived from Table 4 (1.37) and averaging it with a similar value produced using the bar:bench ratio (0.53) from Table 4. Five missing sample values were estimated using this process which scaled estimated values according to the overall sample means of all VT samples.

Field samples from each segment were used to develop a reference table to evaluate the texture and contamination level for each segment. Arithmetic means were used to compute the % <2 mm sediment fraction values (Table 5). Correspondingly, geo-metric means (Gm) were used to calculate the average Pb concentration for each segment (Table 6). The determination of degree of contamination was based on whether or not the geo-mean value for Pb concentration was greater than the PEC. The PEC-quotient (PEC-Q) is a simple way to view the level of a metal in the sediment in relation to its PEC value and is calculated as the measured concentration divided by the PEC value. Quotients above 1 are in the toxic range. Spatial patterns of contamination resulted among the different segments (Table 7). PEC-Q values range from <0.1 to >20 in VT streams. To evaluate the range of variability of contamination, one standard deviation from the geo-mean was used to examine the variability of Pb concentrations (Table 8). However, there was fairly good agreement between the magnitude of the geo-mean itself and its corresponding $+1\sigma$ value. All sites selected as contaminated sites had a geo-mean in excess of the PEC for either one or both of bed and bar deposits. Further, contaminated sites had a plus 1s value at two times the PEC for one or both of bed and bar deposits. Bench concentrations needed to be above the PEC for floodplain soils (345 ppm Pb) to be considered contaminated since they occur at higher elevations out of the aquatic zone. Only one site had a contaminated bench deposit without the bed or bar being contaminated (i.e., 2C lower Crooked Creek). Since the contaminated sediment was not in contact with the water, the segment was judged not to be contaminated. However, benches may be an important storage location for contaminated sediment in some segments and eroded bench sediment could release metal contaminants to the aquatic environment.

<u>Contaminated Stream Segments.</u> Stream segments were considered contaminated if they contained Pb concentrations exceeding 128 ppm in the <2 mm sediment fraction of bed and bar deposits (MacDonald et al., 2000). Recall that the toxicity guidelines used for Cu, Pb, Ni, and Zn in this study are published TEC and PEC values (MacDonald et al., 2000). However, since sediment quality guidelines for cobalt (Co) are not yet published, the Co toxicity threshold used

in this study was estimated based on a TEC of 50 ppm Co from information provided by on-line USEPA Freshwater Sediment Screening Benchmark values (USEPA, 2006).

In total, 42.1 km covering 12 streams were found to be contaminated by Pb in the <2 mm sediment fraction (Table 9; Figure 8). Several other streams had elevated levels of Pb probably due to mining inputs, but the concentrations did not exceed 128 ppm on average. Streams classified as not contaminated by the above criteria include Courtois Creek, Huzzah Creek, Mill Rock Creek, Left Fork Neals Creek, Neals Creek, West Fork-Black River, and Bee Fork (Tables 8 & 9). However, it should be noted that almost all these streams have elevated Pb concentrations above background which are related to mining sources for the most part. Further, although this study found low levels of Pb, sediments in Left Fork Neals Creek exceeded the contamination threshold for Zn.

Logan Creek was marginally contaminated due to averaging effects and low sample density. To address this problem, additional sampling by MDNR was carried out in June 2015 to verify contamination. The results of the additional sampling confirmed contamination in the Logan Creek segment from R-km 64.5 to 59.6 stretching from the Adair Creek to Sweetwater Creek. Only one sample out of the 11 collected within the segment was not contaminated (82 ppm Pb, R-km 63, bench sample) (Appendix I). Average Pb concentrations in the 4.9 km long contaminated segment by sediment type were 164 ppm for the bed, 261 ppm for bars, and 130 ppm for benches. Other Logan Creek segments located upstream (n=6; mean= 8 ppm Pb) and downstream (n=14, mean= 94 ppm Pb) of the contaminated segment were not found to be contaminated. However, the downstream segment extending 1 km below the confluence of Sweetwater Creek (R-km 59.6 to 58.5) had two samples out of 14 total containing Pb at concentrations above the PEC including a bar head sample at R-km 59 with 225 ppm and a bed sample at R-km 58.5 with 153 ppm Pb (Appendix I).

The downstream limits of contaminated stream segments were usually identified directly based on the results of sediment-metal analysis by breaks in measured Pb trends to below the contamination threshold. However, in some cases where sampling access was restricted or sample spacing created gaps in channel coverage, boundaries between contaminated and uncontaminated channel segments were selected based on the location of the mining source points within the drainage network such as just above the most upstream mine or mill discharge point on a stream (Seeger, 2008) or at the confluence of the stream with a tributary or larger river where contaminated sediments would be expected to be mixed and diluted with cleaner sediments inputs to levels below the contaminated threshold (Marcus, 1987).

Contaminated lengths of individual streams vary as expected according to stream size, magnitude of mining inputs, and watershed network factors that control sediment regime and dilution rates, as well as of the result of variations in sampling techniques and sample size (Table 6). Contaminated stream lengths in the VT vary from 0.8 km in Lick Hollow Creek to over

13 km in Crooked Creek. The other 10 streams have contaminated lengths ranging from 1.4 to 5.3 km. Half of the streams had PEC-Q values based on median sample concentrations for the stream between 1 and 2 including Indian Creek, Crooked Creek, Strother Creek, Bills Creek, and Big Creek (Table 6). The most contaminated streams tended to be relatively small and directly draining mining areas such as West Fork Crooked Creek, Lick Hollow Creek, Sweetwater Tributary, and Scoggins Branch. However, PEC-quotients for Sweetwater Creek were relatively high at 3.9 and very high at 18.7 for Adair Creek. Interestingly, not all deposit types were found to contain Pb at levels above the PEC within contaminated segments (Table 10). While the segment can be classified as contaminated with just a bed or bar deposit being found contaminated, the uncontaminated deposits in that segment are not included in contaminated sediment storage calculations later on.

Finer bench deposits tend to contain higher concentrations of Pb compared to bed and bar deposits, but not in all streams. Lead concentrations in benches tend to be similar or lower in Indian Creek, Bills Creek and Bee Fork, and Big Creek (Table 6). Mud-drape deposits on bar surfaces usually contain significant percentages of silt- and clay-sized particles and fine organic matter detritus which can sorb Pb and other metals to relatively high concentrations. In VT streams, mud-drape deposits are finer and more enriched with Pb and other metals compared to adjacent bed deposits. Indeed, Pb concentrations in mud-drapes are typically 5 to 20 times higher than found in nearby bar sediments (Table 11).

Mining source effects on metal toxicity. Previous studies found that elevated Pb concentrations in stream sediments typically decreased to background levels within 12 km of mining sources (Brumbaugh et al., 2007; Lee, 2008). For this study, "near source" samples were collected from sites located within 1 km of mine source points as identified by Seeger (2008) (Table 12). The median and maximum metals concentrations for near-source sediment sample sets were evaluated by the use of PEC-quotient values (Table 13). For proximal or near source sites, the PEC-quotient for median Pb values was above 1 in all streams except Neals Creek, Left Fork Neals Creek, Bee Fork, West Fork-Black River, and Logan Creek (Table 12). Minimum sample concentrations exceeded the PEC-Q in Crooked Creek, Strother Creek, and Sweetwater tributary. Further, PEC-quotients greater than five were found in Crooked Creek, Lick Hollow Creek, Adair Creek, Sweetwater Tributary, Sweetwater Creek, and Scoggins Branch (Table 12).

Other metals concentrations in channel sediments

Toxic levels of median Zn contamination were also found in Strother Creek, Left Fork Neals Creek, Bills Creek, Adair Creek, Scoggins Branch, and Big Creek (Table 12). Median values of near source sites exceeded the PEC for Cu only in Adair Creek, but maximum concentrations exceeded the PEC in Indian and Lick Hollow Creeks. PEC-quotients exceeded 1 for Nickel in Left Fork Neals Creek, Neals Creek, Strother Creek, and Lick Hollow Creek, and for Cobalt in Strother Creek, Bills Creek, and Big Creek (Table 12). To varying degrees, Pb-contaminated streams were contaminated with other metals including Zn, Cu, Co, and Ni (Tables 11 & 12). However, most

streams that were contaminated with other metals are also found to be contaminated with Pb and Pb —contaminated lengths were always longer than or equal to other metals. One exception is Neals Creek and Left Fork Neals Creek which has high Zn, Co, and Ni levels but relatively low sediment Pb concentrations (Table 13). Moreover, near source sediments from Logan Creek, Sweetwater Creek, Bee Fork, and Crooked Creek were only contaminated with Pb (Table 13).

Cadmium concentrations in channel sediments. While not evaluated in this study, previous studies have detected cadmium (Cd) at high concentrations in stream sediments in the VT in the vicinity of mining operations (Gale and Wixon, 1979; Brumbaugh et al., 2007, Lee, 2008). Sediment toxicity thresholds for Cd range from the TEC of 1 ppm to the PEC of 5 ppm Cd (MacDonald et al., 2000). Concentrations of Cd in the <2 mm sediment fraction were above the TEC in Crooked Creek and upper Strother Creek and above the PEC in the West Fork of the Black River below the West Fork Mine (Brumbaugh et al., 2007). In general, the <63 um sediment fraction typically contains Cd concentrations above the TEC within 12 km downstream of mining locations in the VT (Lee, 2008).

Pb-tailings contribution to stream sediments. In the Big River, there is a strong positive relationship among calcium (Ca), inorganic carbon (IC), and Pb (Pavlowsky et al., 2010a). Dolomite is the host rock in the Old Lead Belt with an elemental composition of Ca, Mg (CO₃)₂. Therefore, mill tailings released to the local soils and streams contain high Ca, C, and Pb concentrations that become diluted downstream away from source. This strong relationship indicated that there was a strong contribution of tailings particles as the source of pollution in the Big River. In contrast to the Big River, VT stream sediments show a poor relationship between Pb and Ca in contaminated sediments even though the dolomite host rock is the same for both mining areas (Figure 9). However, as expected, there was a strong relationship between Ca and IC in the <250 um fraction of stream sediments in the VT. Carbon:calcium ratios for dolomite and calcite minerals follow the trend of the sediment relationship and bracket the denser areas of the data scatter (Figure 9). This relationship indicates that there is a carbonate rock or secondary mineral signature in VT stream sediments. However, the lack of a strong relationship to Pb suggests that detrital tailings inputs are not as abundant a source of contamination as in the Big River.

More study is needed to identify the specific source and form of mining-Pb supplied to VT streams. One source of Pb to VT streams is apparently associated with very fine tailings particles that breakdown relatively rapidly in the stream environment or dissolved metals released from drains or seeps around tailings ponds or mill operations which then bind to fine sediments in the stream bed or saturated portions of bar deposits (Seeger, 2008). Nevertheless, Ca concentrations in several samples exceed 10% which is relatively high for stream sediments in general and may indicate local tailings inputs (Figure 11). High Ca concentrations are found in sediments both close and distant to mining discharge points

suggest another source of Ca to stream sediments besides mining inputs. Channel sediments from Indian Creek below the New Viburnum tailings pond and Sweetwater tributary below the Sweetwater pond have high Ca as do sediments from lower Crooked and Neals Creeks which are relatively far away from mining sites (Figure 9). Crooked Creek was affected by acid plant and smelter plant discharges as well as past smelter emissions. Moreover, modern mill technology used in the VT may reduce the impact of tailings releases on Pb contamination compared to the historical mining in the Old Lead Belt (Seeger, 2008). The three tailings samples analyzed from the Old Viburnum Tailings Pond averaged 10% Ca, but only 338 ppm Pb (Table 11). While tailings releases in the VT may provide a source of elevated Pb to stream sediments, other sources maybe be responsible for contamination such as smelter emissions, mine water discharges, tailings pond water seepage, and spilled ores and concentrates along roadways.

Channel Geomorphology Relationships

A geomorphic model is used in this study to predict sediment storage for contaminated segments based on the relationship between active channel width and cross-sectional storage in the VT streams as described in the methods section. Field data on channel morphology and sediment storage from 62 stream sites were used to develop geomorphic relationships to evaluate VT stream storage components and to support the use of active channel width as the primary driver to predict contaminated sediment storage (Appendix G). Drainage area is often used to scale channel form variables for hydrological and geomorphic analysis (Rosgen, 1996; Simon et al, 2004). Best-fit regression equations indicate correlation among channel morphology/storage variables and drainage area (Table 14). Channel width variables ($r^2 = >0.5$) tend to correlate with drainage area more strongly than depth or height variables ($r^2 = 0.2-0.4$). Probe depth refers to the deepest point in the channel marked by refusal on bedrock or coarse channel lag. The difference between the average bed depth and probe depth determines the thickness of bed storage in the channel. The best drainage area-depth relationship is with probe depth (r^2 = 0.413) suggesting that bed storage tends to systematically increase downstream (Table 14). Bench variables in general indicate a poor relationship with drainage area. Bench deposits were not found at 11 of the 62 channel assessment sites. They are frequently subtle or narrow features that may go undetected by field workers, especially in the summer when vegetation obstructs the landscape from view.

Active channel width provides the most significant predictor of total channel sediment storage volume compared to other geomorphic variables such as slope, depth, elevation, and drainage area (Table 15). While these other variables are positively related to storage and are sometimes used to explain storage trends in other studies, channel width provides the best correlation (r^2 =0.910) with drainage area, the second best predictor (r^2 =0.696). The analysis of complex geomorphic-storage relationships is beyond the scope of this study. However, in general, total channel sediment storage in VT streams decreases dramatically when active

channel width is <20 m, reach elevation >300 meters above sea level, drainage area <15 km², and/or exposed bedrock covered >10% of the channel bed.

To better evaluate sediment storage trends in VT stream, the 62 field sites were classified according to drainage area and relative channel width using storage results in Appendix G-1 & 2 (Figures 10 & 11). Five drainage area classes and four width classes were used to display median class values for total sediment storage (m³/m) and percent of total storage that is within bar deposits above the low flow waterline (Bar>WL%). Relative width is defined by the "wide width ratio" (WWR) calculated as active channel width divided by bed width. Given the strong influence of active width on storage, this ratio scales the width of the channel by bed width or low-water channel width. Larger WWR values indicate for a given channel size, more of the channel cross-section would be composed of bar or bench deposits and thus overall storage volume should increase. As expected, total storage increases with both drainage area and WWR (Figure 12). Total sediment storage ranges from <10 m³/m in relatively small and narrow streams to >30 m³/m in larger and wide streams (Figure 11). Similarly, the proportion of bar storage above the waterline increases from around 10% in smaller channels to 30% in larger channels (Figure 11). The distribution of storage in the channel also changes with scale (Figure 11). Bed storage represents about 50% of the total storage in smaller and narrow streams, but decreases in relative contribution to <20% in larger streams (Figure 11). Conversely, bar storage contribution increases from 20-40% in small streams to 60-80% in larger streams (Figure 11).

Channel Sediment and Pb Storage

Active Channel Width-Storage Models. The strong relationship between channel width and sediment storage in VT stream systems is used in this study to calculate contaminated sediment and Pb storage. Active channel width is a good predictor of total storage (r^2 =0.89-0.91, bar storage (r^2 =0.77-0.81), and, to a lesser degree, bed storage (r^2 =0.58) (Table 16). Bench storage produced the poorest correlation with active width (r^2 =0.21-0.44). In order to apply these models to calculate channel sediment storage for contaminated streams, photograph width measurements needed to be converted into field width values to create a similar field width variable as used to develop the model. Channel widths were determined from a series of width measurements at 300 m intervals using 2007 aerial photography of VT streams. Active channel width from 2007 aerial photography is a good predictor of 2012 field-based active width (Appendix G-3 & 4). Width-storage modeling results were used to calculate total-all, bench-top, and Bar>WL sediment volume and Pb mass storage (Figure 12; Appendix G-5 & 6). Average stream segment trends (Tables 5 & 6) developed previously were used to predict Pb content and size for storage volume intervals in order to determine average storage for each contaminated stream (Appendix G-5 & 6).

Channel storage trends by stream. Overall, about 828,500 m³ of contaminated sediment and 206 Mg Pb are stored within the channels of contaminated streams in the VT (Table 17 & Figure 13). Over 80 percent of the contaminated sediment volume is stored in just four streams: Crooked Creek, Strother Creek, Bills Creek, and Sweetwater Creek at segment totals ranging from 136,000 to 218,000 m³ per contaminated stream. Lead mass storage is greatest in Sweetwater Creek (62 Mg) and Crooked Creek (636 Mg) with next highest storage in Bills Creek and Adair Creek at 36 Mg each (Table 17). Five streams have Bar>WL% sediment storage >30% including Strother Creek, Creek, Bills Creek, Sweetwater Creek and Big Creek. Sediment properties vary among the streams evaluated in this study (Tables 4-6). These properties directly influence the calculation of sediment and Pb storage. Further, active channel width measurements and geomorphic models influence the storage outputs of sediment volume and Pb mass greatly (Figures 10 & 12; Appendix G). Future assessments and sampling programs could produce different sets of sediment property relationships given the geomorphic and sediment variability of stream systems in general.

<u>Verification of bar storage depth and contamination</u>. The USGS collected 15 cores from six sites along VT streams to investigate the vertical variability of gravel bar deposits and mining contamination (Smith and Barr, 2015). The coring sites match the locations of bar duplicate sampling sites by MSU for all but one site (Table 18). The cores from the West Fork Black River site sampled by the USGS were from a location several km downstream from the MSU bar sampling site (Appendix D). While the USGS sample size is small compared to the number of VT stream sites used in this study, the data collected by the USGS does appear to preliminarily justify the geomorphic methods used to measure deposits and calculate contaminated storage. The validity of the three important assumptions used in this study to determine bar sediment storage is discussed below.

- 1. Is depth to probe refusal at the deepest point on the stream bed a good indicator of channel bar sediment thickness? Bar depths measured from geomorphic field assessments that are used to calculate bar storage volumes are shorter or equal to those based on stratigraphic determinations of "total sediment depth" in USGS core samples (Table 18). This finding suggests that the "bar heights" used for storage calculations may underestimate the maximum depth of total alluvial sediment storage by one- to two-thirds. According to this limited comparison, the geomorphic assessment used in this study may equal or underestimate actual total lower bar and bench storage and possibly bed storage too, although it was not directly examined by the USGS.
- 2. Does contaminated sediment occur throughout the total thickness of the bar deposit? The "contaminated depths" of the < 2 mm fraction in USGS bar cores are either equal to or slightly longer than bar heights used in this study to determine contaminated storage (Table 18). Contaminated depths in bar cores from Indian Creek and Strother Creek are similar or up to 0.8 m longer than bar heights from the MSU study. However, the greatest differences were found

at the Strother Creek coring site which was not directly sampled during the channel storage assessment phase by MSU. Nevertheless, field bar heights are the same or slightly longer than contaminated core lengths for Bills Creek, Sweetwater Creek, and Logan Creek. The depth of Pb contamination of the <250 um fraction is typically 0.3 m longer than the <2 mm fraction ranging from the same depth to 0.7 m deeper (Table 11). These findings suggest that channel bars are contaminated over the entire bar height as measured during the geomorphic field assessment. Thus, given these limited core samples, contaminated storage volumes estimated from field assessments are representative of core data, but may under-represent actual Pb storage in some cases. Given the results of comparisons between USGS and MSU bar sediment storage and contaminated depths, calculated storage volumes are similar to or less than actual storage at these sites.

3. Are near-surface bar sediment samples collected from a depth of 0.3 m or 1 ft representative of average Pb concentration for the total contaminated thickness of the channel bar? The Pb concentration in the sample from the upper foot or 0.3 m of the core was compared to the average Pb concentration for the entire contaminated portion of the core (Table 19). In general, the ratio of average Pb concentration to top Pb concentration was one and ranged from 0.9 to 1.1. This finding indicates that the Pb concentrations determined from the shallow bar pits used in the storage assessment are good estimators of the average Pb concentration over the entire depth of the contaminated bar. The Pb concentrations for the core samples were determined by XRF analysis of the <2 mm fraction.

Abundance of fine-grained sediment in channel deposits. In this study, the "bulk" sediment is defined as the portion of the total sediment sample collected in the field that passes a 32 mm sieve. Bulk sediment includes the entire volume of contaminated sediment. However, the actual amount of contaminated fine-grained sediment fraction will typically be much less in channel deposits. While toxic thresholds are not published for the <250 um fraction, its contribution to the sediment in the deposit and total Pb burden can be important. The proportion of fine sediment particles within bulk channel bed and bar sediments and their contribution to overall Pb burden in the sediment is variable and generally low (Appendices E 7 F). The average percentage of <250 um particles in bulk sediment ranges from 2-3% in Crooked and Neals Creeks to a high of 73% in Sweetwater Tributary. Low percentages of the <250 um fraction at approximately <15% in the bulk sediment might not even fill the void space within coarser bed deposits. Thus, contamination trends in the <250 um fraction need to be evaluated in the context of their low overall abundance in channel sediment in some streams. Indeed, the percent of <2mm fraction in bulk sediment is typically <40%, but can approach 80% in some segments.

In comparison to bed and bar deposits, bench-top deposits are relatively fine-grained overall with the <2 mm sediment fraction typically representing >80% of the bulk sample and containing Pb concentrations at similar levels as the finer <250 um fraction in bed and bar

sediments (Table 4 & Appendix F). Thus, per unit volume, bench-top deposits will contain more Pb than other coarser channel deposits because they contain a greater amount of finer particles that sorb Pb to much higher concentrations than sand and gravel particles. Even though the fraction of fine-grained sediment may be low in some channel deposits, compared to coarse sediment particles, fine-grained sediments <63 um in diameter tend to be the more mobile for transport, geochemically-active in the aquatic system, and available for uptake by aquatic life (Miller and Orbock-Miller, 2007).

Floodplain Sediment and Pb Storage

<u>Cesium-137 and Pb Profiles.</u> Cesium-137 analysis of 12 cores from VT floodplains indicated the 1963 peak in Cs-137 occurs below the Pb peak in all of them, so contaminated floodplain layers are generally of VT mining age (Appendix H-1 & 2). There are some variations in the vertical relationship between Pb concentration and Cs-137 activity in some cores. Nevertheless, these findings support Pb contamination during the VT mining period since all twelve Cs-137 profiles: (i) peak (1963-64) at greater depths than more recent Pb peaks related to mining sources, and (ii) elevated Pb concentrations do not occur in soil cores before Cs-137 deposition begins in the mid to late 1950s. These trends suggest that Cs-137 accumulation in the floodplain soils generally started before lead deposition from mining sources. Since the first Cs-137 fallout began in the this region in the middle 1950s and peak fallout occurred in the early 1960s, the timing of floodplain contamination with Pb and other metals began in the 1960s in association with the start-up of mining in the Viburnum Trend.

Floodplain Storage Trends. In a manner similar to identifying contaminated stream channel segments, contaminated floodplain segments were also delineated using a threshold of 345 ppm Pb (Appendix H). Overall, contaminated floodplain soils were found along 21.5 km of stream length storing 168,000 m³ of contaminated sediment and 287 Mg of Pb metal (Table 20). Given the criteria used in this study, no contaminated floodplains were identified in Strother Creek, Left Fork Neals Creek, Neals Creek, Bills Creek, West Fork-Black River, and Logan Creek. West Fork Crooked Creek was classified as not contaminated. However, only one core was collected from the lower end of the stream and so further investigation may be needed to verify this result. The depth of contamination in floodplain soil is typically 0.1-0.2 m (Table 21). Contaminated floodplain width is variable and generally ranges from 10-50 m with maximum width at a Big Creek site of over 169 m (Table 21). Presently, one meter of bank erosion can release 5-20% of the Pb mass stored within the channel bed. This is assuming a contaminated floodplain depth of 0.2 meters. Floodplains contaminated to greater depths have the capacity to release more Pb to the stream.

A comparison of contaminated floodplain soil volume and Pb content among streams indicates that Big Creek has the most contaminated floodplain based on all indicators including sediment volume, Pb mass, and unit storage (Table 20). The high magnitude of contaminated floodplain

storage at Big Creek is due to relatively wide floodplains increasing the sediment volume for storage and additional inputs from aerial deposition of Pb from previous smelter operations at Glover. Atmospheric sources are suggested since floodplains along Big Creek are contaminated upstream of Scoggins Branch which is the only water discharge source available. Scoggins Branch also has relatively high floodplain contamination. The Buick Smelter did not affect floodplains of downwind streams such as Left Fork Neals Creek and Strother Creek due to being located at relatively longer distances from the stack. Further, given its headwaters location and forested valleys, the influence of atmospheric deposition of smelter emissions in streams and tributaries may have been limited. Of the other streams, Sweetwater and Crooked Creeks are storing the most contaminated floodplain sediment volume (Table 20). For their limited length, Adair Creek and Sweetwater Tributary also contain relatively high Pb storage in floodplain soils (Table 20).

Summary of Channel and Floodplain Storage by Stream

In the VT, about 828,000 m3 of contaminated sediment is stored in the channel and about 168,000 on floodplains totaling 996,700 m³ with 83% associated with in-channel deposits and the remainder in floodplains. Contaminated sediment is defined differently for channels and floodplains, but from a management perspective, contaminated materials from different sources may be considered similarly for cleanup activities. About three-quarters of the contaminated floodplain soils are stored in Crooked Creek, and Sweetwater Creek, and Big Creek (Table 22). However, in these streams, in-channel storages typically represent >80% of the total contaminated sediment volume. Big Creek contains the highest volume of contaminated floodplain sediment storage due to aerial deposition from the Glover smelter at 54,000 m³ (Table 22). The total mass of Pb stored within alluvial deposits in VT streams is 667 Mg with 57% in channel sediments and 43% in floodplain soils (Table 22). About two-thirds of the Pb mass is stored in Big Creek, Sweetwater Creek, and Adair Creek. As expected, Big Creek contains the most Pb in floodplain storage at 137 Mg. The Logan Creek watershed including Adair Creek, Sweetwater Tributary, and Sweetwater Creek is currently storing about onequarter of the contaminated sediment volume and almost one-half of the metal mass in the VT stream system.

Contaminated sediment and Pb storage in floodplain deposits represents a potential long-term source of Pb contamination to the riparian ecosystem and stream itself. Bank erosion and soil weathering can release floodplain stored Pb to the stream for periods of 10 to 100 years after mining pollution has ceased (Lewin et al., 1977). Recovery requires a reduction of present and new mining sources to limit future problems as well as sediment controls. The management of contaminated sediment in VT streams needs to focus on tracking fine-grained sediment deposition and remobilization in the channel and floodplain. Assuming that erosion rates of upland soils are localized or managed, geomorphic behavior is largely controlled by hydrologic events, coarse sediment regime, and medium-term bed and bank stability (Martin and

Pavlowsky, 2011). While the fine-grained sediment is contaminated, coarse-grained sediment dynamics control the stability of the stream channel and can create storage sites or sources for finer sediment. Geomorphic processes control the location of contaminant storages through channel planform adjustments and responses to disturbance. The rate of release of metals from channel bar and floodplain storage in the VT is presently unknown. However an understanding of the spatial distribution and rates of remobilization of contaminated sediment is required to understand the recovery rate of VT streams. Further, the influence of climate change and land management on flood regime and geomorphic activity will also influence the stability of VT streams in the future.

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TABLES

Table 1. Mining history for the Viburnum Trend (after Seeger, 2008)

Mine and Mill Name	Mining	History	Desciving Street
(by watershed)	Open	Close	Receiving Stream
Indian Creek			
Viburnum No. 27 mine	1960	1978	Mill Rock Creek*
Viburnum No. 28 mine	1962	2004	Indian Creek
Central Mill near No. 28 mine	1961	2000	Indian Creek
Old Viburnum Pond (1960-1975)			
New Viburnum Pond (1975-2000)			
Viburnum No. 29 mine	1964	open	Indian Creek
Crooked Creek			
Casteel mine/Viburnum No. 35 mine	1983	open	Crooked Creek
Buick Smelter	1967	1991	Crooked & West Fork Crooked Creeks
Buick Resource Recovery Facility	1991	open	Crooked & West Fork Crooked Creeks
Strother Creek			
Magmont mine	1968	1994	Neals Creek & Crooked Creek
Buick mine & mill	1969	open	Strother Creek
West Fork Black River			
Fletcher mine & mill	1966	open	Bee Fork
Brushy Creek mine & mill	1973	open	Lick Creek Hollow & Bills Creek
West Fork mine & mill	1985	Inactive [#]	West Fork Black River
Logan Creek			
Sweetwater mine & mill	1968	open	Adair Creek & Sweetwater Creek
Big Creek			
Glover Smelter	1968	2002	Scoggins Branch & Big Creek

^{*} Mill Rock Creek sediment was sampled for this study but was not considered for further study.

[#] Mining was suspended but the facility remained open in 2012.

Table 2: Correction ratios for split bar samples

	USGS-ICI	P:MSU-XRF Co	rrection ratios		
	Pb	Zn	Cu	Со	Ni
<2 mm se	diment fracti	on			
Mean	0.72	0.86	<u>1.40</u>	<u>0.61</u>	<u>1.20</u>
Stdev	0.12	0.22	0.07	0.22	0.15
Cv%	16	25	5	36	12
Count	9	9	4	6	4
<250 um s	ediment frac	tion			
Mean	0.66	0.60	<u>1.55</u>	0.42	<u>1.08</u>
Stdev	0.11	0.19	0.20	0.19	0.54
Cv%	16	31	13	46	50
Count	10	10	5	8	8

Table 3: Sediment toxicity criteria for VT stream sediments

		Sediment ^a	Floodplain soil ^b
Metal		fine sediment	<2 mm fraction
	TEC	PEC	PEC
Pb	35.8	128	345
Zn	121	459	
Cu	31.6	149	
Ni	22.7	48.6	
Co ^c	Х	50	

^a Reported by MacDonald et al., 2000 for Pb, Zn, Cu, & Ni.

^b Reported by Holmes and Lipton (2014)

^c PEC for Co is approximate value from USEPA (2006).

Table 4: Distribution of grain-size properties and Pb concentrations in VT streams

A) Sediment Texture

Descriptive		% <2 m	m bulk		% <250 (um bulk
Statistic	BED	BAR	BENCH	FP SOIL	BED	BAR
mean	<u>30</u>	<u>41</u>	<u>78</u>	<u>72</u>	<u>6</u>	<u>8</u>
S	20.0	24.9	22.5	22.2	12.2	10.7
RSD%	67.1	61.1	28.9	30.8	210	140
max	98	99	99	100	73	72
95%	83	95	98	98	16	24
75%	33	51	96	92	4.7	8.7
<u>50%</u>	<u>26</u>	<u>33</u>	<u>86</u>	<u>78</u>	<u>2.3</u>	<u>3.8</u>
25%	18	24	68	55	1.4	1.8
5%	8	12	28	30	0.4	0.6
min	4	3	24	18	0.2	0.2
n	73	141	89	497	69	135

B) Sediment Lead Concentration (ppm)

Descriptive		<2 mm	fraction		<250 um	fraction
Statistic	BED	BAR	BENCH	FP SOIL	BED	BAR
Geo-mean	<u>141</u>	<u>51</u>	<u>144</u>	<u>90</u>	<u>336</u>	<u>113</u>
Log s	0.66	0.66	0.79	0.75	0.66	0.64
Geo-RSD%	30.7	38.5	36.8	38.6	26.2	31.1
Max	4,230	6,916	11,804	10,264	6,003	10,770
95%	1830	650	5615	3025	4233	1307
75%	326	122	269	225	1096	304
<u>50%</u>	<u>151</u>	<u>49</u>	<u>113</u>	<u>77</u>	<u>370</u>	<u>108</u>
25%	53	21	49	29	114	38
5%	bd	bd	bd	bd	bd	18
min	bd	bd	bd	bd	bd	bd
n	73	145	89	498	73	145

Table 5: Mean grain-size values for each deposit type and stream segment.

	Stream Segme	ent	Be	d Sedin	nent	Ba	r Sedim	ent	Ben	ch Sedi	ment
ID No.	Name	R-km	n	mean	RSD%	n	mean	RSD%	n	mean	RSD%
1A	Indian Ck	9 to 5.6	3	27	99	2	35	28	4	79	33
1B	Indian Ck	5.6 to 0.8	4	41	74	8	40	50	6	81	17
1C	Indian Ck	0.8 to 0	3	40	93	3	34	40	1	85	х
1D	Courtois Ck	49.6 to 44.9	2	30	20	9	24	47	7	72	42
2A	WF Crooked Ck	2 to 0	2	27	3	no so	imples (4	3%) ^a	1	93	х
2B	Crooked Ck	16 to 2.5	7	21	70	7	45	45	no s	samples (78%)
2C	Crooked Ck	2.5 to 0	3	20	61	3	30	23	7	72	33
3A	LF-Neals Ck	1 to 0	1	33	Х	2	16	2	4	80	13
3B	Neals Ck	10 to 1.5	3	19	64	9	23	53	7	72	35
3C	Strother Ck	11.5 to 6.2	6	26	49	8	31	48	6	57	50
3D	Strother Ck	6.2 to 0	4	17	60	10	42	56	5	72	34
3E	Middle Fork-BR	28.9 to 9.3	1	34	Х	6	43	77	4	83	16
4A	Bills Ck	3.3	1	17	Х	2	15	32	1	98	Х
4B	Lick Hollow	0.8 to 0	no s	samples (24%)	1	24	Х	1	79	х
4C	Bills Ck	3 to 0	4	25	24	4	52	57	1	97	х
4D	Bee Fork	14.5 to 9.1	4	41	95	9	45	65	5	84	35
4E	Bee Fork	9.1 to 0	2	22	10	7	45	81	4	97	1
4F	West Fork-BR	42.6 to 14.1	5	23	69	13	48	76	2	63	82
5A	Adair Ck	1.5 to 0	4	23	21	2	41	15	6	83	21
5B	Sweetwater Ck	4.7 to 3.7	no s	samples (29%)	3	35	46	1	83	х
5C	Sweetwater Trib	1.4 to 0	1	83	Х	no s	samples (65%)	2	40	41
5D	Sweetwater Ck	3.7 to 2.4	3	58	43	4	64	24	2	86	1
5E	Sweetwater Ck	2.4 to 0	2	31	6	8	33	40	1	99	х
5F	Logan Ck	66.5 to 64.5	2	nc	l ^a	2	no	b	2	no	k
5G	Logan Ck	64.5 to 59.6	6	38	81	10	50	32	7	80	15
5H	Logan Ck	59.6 to 58.5	3	n	d	8	no	b	3	no	k
51	Logan Ck	58.5 to 30.7	1	44	х	5	45	41	1	58	х
6A	Big Ck	52.1 to 48.1	1	35	х	8	46	58	1	97	х
6B	Scoggins Br	0.2 to 0	2	28	11	1	23	Х	1	93	Х
6C	Big Ck	48.1 to 46.5	1	30	х	2	60	47	1	97	Х
6D	Big Ck	46.5 to 42.8	1	21	х	3	96	4	2	98	1

^a grain-size not measured in the sample.

The number in parentheses is an estimate of grain-size with the procedure described in the text.

Table 6. Geo-means for Pb in the <2 mm fraction by deposit type and stream segment.

	Stream Segme	nt	Ве	d Sedin	nent	Ba	r Sedim	ent	Ben	Bench Sediment		
ID No.	Name	R-km	n	Gm	RSD%	n	Gm	RSD%	n	Gm	RSD%	
1A	Indian Ck	9 to 5.6	3	158	23.6	2	166	7.3	4	280	8.6	
1B	Indian Ck	5.6 to 0.8	4	82	10.0	8	62	11.2	6	273	12.1	
1C	Indian Ck	0.8 to 0	3	192	9.7	3	104	5.3	1	106	х	
1D	Courtois Ck	49.6 to 44.9	2	21	14.9	9	26	26.8	7	64	22.4	
2A	WF Crooked Ck	2 to 0	2	991	0.1	no so	amples (4	176) ^a	1	4,854	Х	
2B	Crooked Ck	16 to 2.5	7	381	15.6	7	208	18.5	no .	samples ((488)	
2C	Crooked Ck	2.5 to 0	3	74	14.2	3	68	19.6	7	490	21.1	
3A	LF-Neals Ck	1 to 0	1	94	Х	2	45	3.9	4	103	26.9	
3B	Neals Ck	10 to 1.5	3	30	13.2	9	27	21.7	7	64	22.1	
3C	Strother Ck	11.5 to 6.2	6	214	8.4	8	185	8.9	6	139	9.6	
3D	Strother Ck	6.2 to 0	4	68	21.1	10	21	36.2	5	53	27.3	
3E	Middle Fork-BR	28.9 to 9.3	1	<dl< td=""><td>х</td><td>6</td><td><dl< td=""><td>32.5</td><td>4</td><td>18</td><td>23.2</td></dl<></td></dl<>	х	6	<dl< td=""><td>32.5</td><td>4</td><td>18</td><td>23.2</td></dl<>	32.5	4	18	23.2	
4A	Bills Ck	3.3	1	48	х	2	<dl< td=""><td>16.2</td><td>1</td><td>22</td><td>х</td></dl<>	16.2	1	22	х	
4B	Lick Hollow	0.8 to 0	no s	amples (9	9,568)	1	6,916	Х	1	48	Х	
4C	Bills Ck	3 to 0	4	106	17.4	4	158	17.2	1	76	Х	
4D	Bee Fork	14.5 to 9.1	4	125	15.2	9	75	15.3	5	56	20.9	
4E	Bee Fork	9.1 to 0	2	<dl< td=""><td>0.0</td><td>7</td><td><dl< td=""><td>30.1</td><td>4</td><td><dl< td=""><td>19.2</td></dl<></td></dl<></td></dl<>	0.0	7	<dl< td=""><td>30.1</td><td>4</td><td><dl< td=""><td>19.2</td></dl<></td></dl<>	30.1	4	<dl< td=""><td>19.2</td></dl<>	19.2	
4F	West Fork-BR	42.6 to 14.1	5	20	33.6	13	<dl< td=""><td>36.0</td><td>2</td><td>24</td><td>38.5</td></dl<>	36.0	2	24	38.5	
5A	Adair Ck	1.5 to 0	4	2096	10.8	2	549	36.4	6	7399	3.5	
5B	Sweetwater Ck	4.7 to 3.7	no.	samples	(<dl)< td=""><td>3</td><td><dl< td=""><td>46.2</td><td>1</td><td><dl< td=""><td>Х</td></dl<></td></dl<></td></dl)<>	3	<dl< td=""><td>46.2</td><td>1</td><td><dl< td=""><td>Х</td></dl<></td></dl<>	46.2	1	<dl< td=""><td>Х</td></dl<>	Х	
5C	Sweetwater Trib	1.4 to 0	1	2,629	Х	no s	amples (6	516%)	2	762	40.7	
5D	Sweetwater Ck	3.7 to 2.4	3	398	7.3	4	482	5.1	2	2985	2.5	
5E	Sweetwater Ck	2.4 to 0	2	357	9.9	8	476	18.5	1	415	Х	
5F	Logan Ck	66.5 to 64.5	2	<dl< td=""><td>8.8</td><td>2</td><td><dl< td=""><td>18.5</td><td>2</td><td><dl< td=""><td>28.2</td></dl<></td></dl<></td></dl<>	8.8	2	<dl< td=""><td>18.5</td><td>2</td><td><dl< td=""><td>28.2</td></dl<></td></dl<>	18.5	2	<dl< td=""><td>28.2</td></dl<>	28.2	
5G	Logan Ck	64.5 to 59.6	6	283	14.3	10	75	24.2	7	109	19.5	
5H	Logan Ck	59.6 to 58.5	3	75	14.3	8	91	11.0	3	75	11.2	
51	Logan Ck	58.5 to 30.7	1	59	Х	5	21	20.8	1	199	Х	
6A	Big Ck	52.1 to 48.1	1	30	Х	8	22	15.9	1	109	Х	
6B	Scoggins Br	0.2 to 0	2	1296	5.5	1	2,053	х	1	3,231	Х	
6C	Big Ck	48.1 to 46.5	1	185	х	2	266	20.1	1	210	Х	
6D	Big Ck	46.5 to 42.8	1	45	Х	3	66	11.4	2	113	0.1	

^a grain-size not measured in the sample.

The number in parentheses is an estimate of grain-size with the procedure described in the text.

Table 7. Log-normal distribution of PEC quotient values for stream segments.

Color key:

Background Range

PEC-Q >1

PEC-Q >2

PEC-Q >5

	Stream Segme	ent	Bed (P	EC = 128 p	pm Pb)	Bar (Pi	EC = 128 p	pm Pb)	Bench (PEC = 345	ppm Pb)
ID No.	Name	R-km	-1s	Gm ^a	+1s	-1s	Gm	+1s	-1s	Gm	+1s
1A	Indian Ck	9 to 5.6	0.4	1.2	4.1	0.9	1.3	1.9	0.5	0.8	1.3
1B	Indian Ck	5.6 to 0.8	0.4	0.6	1.0	0.3	0.5	0.8	0.4	0.8	1.6
1C	Indian Ck	0.8 to 0	0.9	1.5	2.5	0.6	0.8	1.0		0.3 ^b	
1D	Courtois Ck	49.6 to 44.9	0.1	0.2	0.3	0.1	0.2	0.5	0.1	0.2	0.5
2A	WF Crooked Ck	2 to 0	7.7	7.7	7.8		no samples			14.1	
2B	Crooked Ck	16 to 2.5	1.2	3.0	7.5	0.6	1.6	4.4		no samples	
2C	Crooked Ck	2.5 to 0	0.3	0.6	1.1	0.2	0.5	1.2	0.4	1.4	5.3
3A	LF-Neals Ck	1 to 0		0.7		0.3	0.4	0.4	0.1	0.3	1.0
3B	Neals Ck	10 to 1.5	0.2	0.2	0.4	0.1	0.2	0.4	0.1	0.2	0.5
3C	Strother Ck	11.5 to 6.2	1.1	1.7	2.6	0.9	1.4	2.3	0.3	0.4	0.6
3D	Strother Ck	6.2 to 0	0.2	0.5	1.3	0.1	0.2	0.5	0.1	0.2	0.5
3E	Middle Fork-BR	28.9 to 9.3		0.1		0.04	0.1	0.2	0.03	0.1	0.1
4A	Bills Ck	3.3		0.4		0.1	0.1	0.1		0.1	
4B	Lick Hollow	0.8 to 0		no samples			54			0.1	
4C	Bills Ck	3 to 0	0.4	0.8	1.9	0.5	1.2	3.0		0.2	
4D	Bee Fork	14.5 to 9.1	0.5	1.0	2.0	0.3	0.6	1.1	0.1	0.2	0.4
4E	Bee Fork	9.1 to 0	0.1	0.1	0.1	0.04	0.1	0.2	0.02	0.04	0.1
4F	West Fork-BR	42.6 to 14.1	0.1	0.2	0.4	0.03	0.1	0.2	0.02	0.1	0.2
5A	Adair Ck	1.5 to 0	7.2	16.4	37.5	0.4	4.3	42.6	15.7	21.4	29.3
5B	Sweetwater Ck	4.7 to 3.7		no samples		0.03	0.1	0.3		0.03	
5C	Sweetwater Trib	1.4 to 0		20.5			no samples		0.1	2.2	32.8
5D	Sweetwater Ck	3.7 to 2.4	2.0	3.1	4.8	2.8	3.8	5.1	7.1	8.7	10.6
5E	Sweetwater Ck	2.4 to 0	1.6	2.8	5.0	1.2	3.7	11.7		1.2	
5F	Logan Ck	66.5 to 64.5	0.03	0.04	0.04	0.04	0.1	0.1	0.01	0.02	0.04
5G	Logan Ck	64.5 to 59.6	1.0	2.2	5.0	0.2	0.6	1.7	0.1	0.3	0.8
5H	Logan Ck	59.6 to 58.5	0.3	0.6	1.1	0.4	0.7	1.2		0.2	
51	Logan Ck	58.5 to 30.7		0.5		0.1	0.2	0.3		0.6	
6A	Big Ck	52.1 to 48.1		0.2		0.1	0.2	0.3		0.3	
6B	Scoggins Br	0.2 to 0	6.8	10.1	15.0		16			9.4	
6C	Big Ck	48.1 to 46.5		1.4		0.7	2.1	6.4		0.6	
6D	Big Ck	46.5 to 42.8		0.3		0.3	0.5	0.8	0.3	0.3	0.3

^a Gm= geometric mean plus and minus geometric standard deviation (mean and s for logged values)

^b When just a single Gm value is displayed, only one sample was collected for that deposit type in the segment.

Table 8. Classification of contaminated stream segments

	Stream Segme	ent	Length	Geom	nean Pb	> PEC	+1s va	alue > 2	x PEC	Contam.
ID No.	Name	R-km	km	Bed	Bar	Bench	Bed	Bar	Bench	Segment?
1A	Indian Ck	9 to 5.6	3.4							YES ^a
1B	Indian Ck	5.6 to 0.8	4.8							
1C	Indian Ck	0.8 to 0	0.8							YES
1D	Courtois Ck	49.6 to 44.9	4.7							
2A	WF Crooked Ck	2 to 0	2		, p			?		YES
2B	Crooked Ck	16 to 2.5	13.5			?			?	YES
2C	Crooked Ck	2.5 to 0	2.5							bench ^c
3A	LF-Neals Ck	1 to 0	1							
3B	Neals Ck	10 to 1.5	8.5							
3C	Strother Ck	11.5 to 6.2	5.3							YES
3D	Strother Ck	6.2 to 0	6.2							
3E	Middle Fork-BR	28.9 to 9.3	19.6							
4A	Bills Ck	3.5 to 3	0.5							
4B	Lick Hollow	0.8 to 0	0.8	?			?			YES
4C	Bills Ck	3 to 0	3							YES
4D	Bee Fork	14.5 to 9.1	5.4							
4E	Bee Fork	9.1 to 0	9.1							
4F	West Fork-BR	42.6 to 14.1	28.5							
5A	Adair Ck	1.5 to 0	1.5							YES
5B	Sweetwater Ck	4.7 to 3.7	1							
5C	Sweetwater Trib	1.4 to 0	1.4		?		?	?		YES
5D	Sweetwater Ck	3.7 to 2.4	1.3							YES
5E	Sweetwater Ck	2.4 to 0	2.4							YES
5F	Logan Ck	66.5 to 64.5	2							
5G	Logan Ck	64.5 to 59.6	4.9							YES
5H	Logan Ck	59.6 to 58.5	1.1							
51	Logan Ck	58.5 to 30.7	27.8							
6A	Big Ck	52.1 to 48.1	4							
6B	Scoggins Br	0.2 to 0	0.2					?	?	YES
6C	Big Ck	48.1 to 46.5	1.6							YES
6D	Big Ck	46.5 to 42.8	3.7							

^a Meets criteria based on Gm value exceeding the PEC for bed or bar sediment samples.

^b ?, no sample collected, but assumed to be contaminated given high Pb in other deposits.

^c Surface bench deposits are contaminated, but not bed or bar sediments.

 Table 9. Inventory of uncontaminated and contaminated stream segments

Stungare	Bed and Bar Sed	liments < Pb PEC	Contam	inated Segmer	nts
Stream	ID No.	Length (km)	ID No.	Length (km)	%
Indian Ck	1B	4.8	1A & 1C	4.2	10.0
Courtois Ck	1D	4.7			
WF Crooked Ck			2A	2	4.8
Crooked Ck	2C	2.5	2B	13.5	32.1
LF-Neals Ck	3A	1			
Neals Ck	3B	8.5			
Strother Ck	3D	6.2	3C	5.3	12.6
Middle Fork-Black R	3E	19.6			
Bills Creek	4A	0.5	4C	3	7.1
Lick Hollow			4B	0.8	1.9
Bee Fork	4D & 4E	14.5			
West Fork-Black R	4F	28.5			
Adair Ck			5A	1.5	3.6
Sweetwater Ck	5B	1	5D & 5E	3.7	8.8
Sweetwater Tributary			5C	1.4	3.3
Logan Ck	5F, 5H, & 5I	30.9	5G	4.9	11.6
Big Ck	6A & 6D	7.7	6C	1.6	3.8
Scoggins Br			6B	0.2	0.5
Totals	n= 17	130.4	n= 14	42.1	100

Table 10. Contaminated stream segments used for contaminated sediment storage analysis.^a

	Stream Segme	ent	Length	Geon	nean Pb (ppm)
ID No.	Name	R-km	km	Bed	Bar	Bench
1A	Indian Ck	9 to 5.6	3.4	158	166	280
1C	Indian Ck	0.8 to 0	0.8	192	104	106
2A	WF Crooked Ck	2 to 0	2	991	(476)	4,854
2B	Crooked Ck	16 to 2.5	13.5	381	208	(488)
3C	Strother Ck	11.5 to 6.2	5.3	214	185	139
4B	Lick Hollow	0.8 to 0	0.8	(9,568)	6,916	48
4C	Bills Ck	3 to 0	3	106	158	76
5A	Adair Ck	1.5 to 0	1.5	2,096	549	7,399
5C	Sweetwater Trib	1.4 to 0	1.4	2,629	(616)	762
5D	Sweetwater Ck	3.7 to 2.4	1.3	398	482	2,985
5E	Sweetwater Ck	2.4 to 0	2.4	357	476	415
5G	Logan Ck	64.5 to 59.6	4.9	283	75	109
6B	Scoggins Br	0.2 to 0	0.2	1,296	2,053	3,232
6C	Big Ck	48.1 to 46.5	1.6	185	266	210

^a Shaded boxes indicate a contaminated deposit.

Uncontaminated deposits were not included in storage analysis.

Table 11: Metal concentrations in soil, mill tailings, and mud-drape deposits.

				. 3	_	_	_		_		_
Sample T	ype	n	<2mm	Pb ^a	Zn	Cu	Со	Ni	Fe	Mn	Ca
•			%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
				r							
Smelter soil	0-5 cm	4	79	3,939	329	143	ND^{b}	23	10,733	549	1,087
(depth)	15-20 cm	4	76	473	40	21	ND	ND	10,152	126	ND
Old Vib. Pond	Tailings	3	75	338	276	165	ND	ND	12,448	316	100,661
Indian Ck 0.2	Mud-drape	1	75	600	728	137	24	20	15,438	918	21,525
	Bar	2	33	101	222	45	ND	ND	12,944	377	14,796
Bee Fork 10.6	Mud-drape	1	61	1,315	290	ND	81	47	20,010	2,892	7,895
	Bar	1	96	160	73	ND	ND	26	10,348	770	1,313
Bee Fork 14.2	Mud-drape	1	49	1,418	316	32	77	73	20,760	2,813	6,564
	Bar	1	84	87	29	ND	ND	ND	7,978	229	709
Bee Fork 15.4	Mud-drape	1	95	63	80	ND	49	16	19,393	1,912	3,324
	Bar	1	78	11	12	ND	ND	ND	8,867	358	1,119
West Fork 35.6	Mud	1	81	514	280	ND	34	34	16,497	1,417	5,142
	Bar	1	12	23	42	ND	ND	12	8,431	190	406
Black River	Mud-drape	1	72	38	61	ND	27	ND	15,587	1,095	433
	Bar	2	49	ND	12	ND	ND	ND	7,959	97	ND
Sweetwater 1.9	Mud-drape	1	66	737	111	25	34	18	17,000	597	945
	Bar	6	39	684	162	48	ND	ND	10,529	532	3,081
Sweetwater 3.3	Mud-drape	1	88	11,377	1,045	374	61	19	18,140	1,560	10,349
	Bar	2	67	589	88	ND	ND	ND	8,456	320	4,032
Big Ck 50.4	Mud-drape	1	94	46	44	ND	ND	ND	18,775	809	ND
	Bar	3	77	35	24	ND	38	17	21,694	720	ND

^a median value of corrected XRF analyses

^b ND, no detection: indicates a value that is below the detection limit

Table 12: Corrected metal concentrations for channel sediments within 1 km of mining sites.

Indian Creek

<2 mm	Pb	Zn	Cu	Со	Ni
Max	455	547	333	40	44
Median	<u>125</u>	<u>295</u>	<u>32</u>	<u>8</u>	<u>ND</u>
Min	43	30	ND	ND	ND
Sample n	16	16	16	16	16
No. ND	0	0	2	8	15

<250 um	Pb	Zn	Cu	Со	Ni
Max	1,779	1,553	1,113	109	70
Median	<u>316</u>	<u>364</u>	<u>113</u>	<u>ND</u>	<u>ND</u>
Min	116	64	ND	ND	ND
Sample n	15	15	15	15	15
No. ND	0	0	1	12	11

Crooked Creek

<2 mm	Pb	Zn	Cu	Со	Ni
Max	1,190	293	113	42	20
Median	<u>994</u>	<u>152</u>	<u>36</u>	<u>20</u>	<u>ND</u>
Min	286	71	ND	ND	ND
Sample n	7	7	7	7	7
No. ND	0	0	1	3	5

<250 um	Pb	Zn	Cu	Со	Ni
Max	4,330	413	423	34	40
Median	<u>1,998</u>	<u>239</u>	<u>149</u>	<u>ND</u>	<u>19</u>
Min	701	104	34	ND	ND
Sample n	7	7	7	7	7
No. ND	0	0	0	5	2

Neals Creek and Left Fork

<2 mm	Pb	Zn	Cu	Со	Ni
Max	94	1,365	ND	102	318
Median	<u>50</u>	<u>415</u>	<u>ND</u>	<u>32</u>	<u>90</u>
Min	30	126	ND	ND	19
Sample n	5	5	5	5	5
No. ND	0	0	5	1	0

<250 um	Pb	Zn	Cu	Со	Ni
Max	201	1,901	20	76	570
Median	<u>84</u>	<u>433</u>	<u>ND</u>	<u>29</u>	<u>127</u>
Min	56	501	ND	ND	23
Sample n	5	5	5	5	5
No. ND	0	0	4	2	0

Strother Creek

<2 mm	Pb	Zn	Cu	Со	Ni
Max	282	797	ND	295	365
Median	<u>158</u>	<u>720</u>	<u>ND</u>	<u>210</u>	<u>274</u>
Min	145	585	ND	204	230
Sample n	3	3	3	3	3
No. ND	0	0	3	0	0

<250 um	Pb	Zn	Cu	Со	Ni
Max	1,189	2,867	ND	946	1,700
Median	<u>424</u>	<u>1,174</u>	<u>ND</u>	<u>441</u>	<u>630</u>
Min	351	688	ND	177	231
Sample n	3	3	3	3	3
No. ND	0	0	3	0	0

Bills and Lick Hollow Creeks

<2 mm	Pb	Zn	Cu	Со	Ni
Max	6,916	14,208	260	737	1,284
Median	<u>290</u>	<u>704</u>	<u>8</u>	<u>82</u>	<u>59</u>
Min	87	176	ND	ND	ND
Sample n	4	4	4	4	4
No. ND	0	0	2	1	1

<250 um	Pb	Zn	Cu	Со	Ni
Max	10,770	15,923	173	812	1,719
Median	<u>564</u>	<u>828</u>	<u>ND</u>	<u>61</u>	<u>99</u>
Min	127	166	ND	13	16
Sample n	4	4	4	4	4
No. ND	0	0	3	0	0

Bee Fork

<2 mm	Pb	Zn	Cu	Со	Ni
Max	153	79	ND	ND	19
Median	<u>107</u>	<u>41</u>	<u>ND</u>	<u>ND</u>	<u>11</u>
Min	75	29	ND	ND	ND
Sample n	6	6	6	6	6
No. ND	0	0	6	6	2

<250 um	Pb	Zn	Cu	Со	Ni
Max	679	146	ND	16	28
Median	<u>233</u>	<u>62</u>	<u>ND</u>	<u>ND</u>	<u>24</u>
Min	139	53	ND	ND	13
Sample n	6	6	6	6	6
No. ND	0	0	6	4	0

Table 12 (con't)

West Fork-Black River

<2 mm	Pb	Zn	Cu	Со	Ni
Max	63	336	ND	63	83
Median	<u>59</u>	<u>223</u>	<u>ND</u>	<u>32</u>	<u>41</u>
Min	54	110	ND	ND	ND
Sample n	2	2	2	2	2
No. ND	0	0	2	1	1

<250 um	Pb	Zn	Cu	Со	Ni
Max	265	1,166	ND	155	315
Median	<u>211</u>	<u>671</u>	<u>ND</u>	<u>54</u>	<u>170</u>
Min	156	175	ND	ND	25
Sample n	2	2	2	2	2
No. ND	0	0	2	1	0

Adair Creek

<2 mm	Pb	Zn	Cu	Со	Ni
Max	4,230	2,141	217	30	48
Median	<u>3,423</u>	<u>1,664</u>	<u>146</u>	<u>ND</u>	<u>25</u>
Min	108	22	ND	ND	ND
Sample n	3	3	3	3	3
No. ND	0	0	1	2	1

<250 um	Pb	Zn	Cu	Со	Ni
Max	6,003	2,356	304	16	63
Median	<u>4,968</u>	<u>1,747</u>	<u>240</u>	<u>ND</u>	<u>45</u>
Min	252	89	ND	ND	ND
Sample n	3	3	3	3	3
No. ND	0	0	1	2	1

Sweetwater Creek and Tributary

<2 mm	Pb	Zn	Cu	Со	Ni
Max	2,629	400	76	35	ND
Median	<u>539</u>	<u>102</u>	<u>10</u>	<u>ND</u>	<u>ND</u>
Min	238	45	ND	ND	ND
Sample n	15	15	15	15 15	
No. ND	0	0	7	12	15

<250 um	Pb	Zn	Cu Co		Ni
Max	3,350	352	175	28	ND
Median	<u>1,214</u>	<u>184</u>	<u>55</u>	<u>ND</u>	<u>ND</u>
Min	370	46	ND	ND	ND
Sample n	14	14	14	14	14
No. ND	0	0	2	9	14

Logan Creek

<2 mm	Pb	Zn	Cu	Со	Ni
Max	182	221	ND	40	18
Median	<u>116</u>	<u>102</u>	ND 13		<u>ND</u>
Min	45	71	ND	ND	ND
Sample n	4	4	4	4	4
No. ND	0	0	4	2	3

<250 um	Pb	Zn	Cu	Со	Ni
Max	360	200	17	ND	ND
Median	<u>258</u>	<u>135</u>	<u>14</u>	<u>ND</u>	<u>ND</u>
Min	134	85	ND	ND	ND
Sample n	4	4	4	4	4
No. ND	0	0	1	4	4

Big Creek and Scoggins Branch

<2 mm	Pb	Zn	Zn Cu		Ni	
Max	2,053	6,921	106	254	74	
Median	<u>785</u>	<u>2,081</u>	<u>7</u>	<u>56</u>	<u>ND</u>	
Min	120	390	ND	ND	ND	
Sample n	6	6	6	6	6	
No. ND	0	0	3	1	5	

<250 um	Pb	Zn	Cu	Со	Ni
Max	4,168	10,757	304	312	140
Median	<u>1,991</u>	<u>2,608</u>	<u>107</u>	<u>74</u>	<u>27</u>
Min	261	1,206	ND	31	ND
Sample n	6	6	6	6	6
No. ND	0	0	2	0	2

Table 13: PEC-Quotients for channel sediments within 1 km of mining sources

A) PEC-Quotients for Pb

Chungun	-		Pb	
Stream	n	min	R50%	max
Indian Creek	16	0.3	1	3.6
Crooked Creek	7	2.2	7.8	9.3
Neals Creek/Left Fork	5	0.2	0.4	0.7
Strother Creek	3	1.1	1.2	2.2
Bills/Lick Hollow Creeks	4	0.7	2.3	54
Bee Fork	6	0.6	0.8	1.2
West Fork-Black River	2	0.4	0.5	0.6
Adair Creek	3	0.8	29.9	33
Sweetwater Creek/Tributary	15	1.9	4.2	20.5
Logan Creek	4	0.4	0.9	1.4
Big Creek/Scoggins Branch	6	0.9	6.1	16





B) PEC-Quotients for Zn, Cu, Co, & Ni

Chuo ama	Z	n	С	u	С	0	N	li
Stream	R50%	max	R50%	max	R50%	max	R50%	max
Indian Creek	0.6	1.2	0.2	2.2	0.2	0.8	ND	0.9
Crooked Creek	0.3	0.6	0.2	0.8	0.4	0.8	ND	0.4
Neals Creek/Left Fork	0.9	3	ND	ND	0.6	2	1.9	6.5
Strother Creek	1.6	1.7	ND	ND	4.2	5.9	5.6	7.5
Bills/Lick Hollow Creeks	1.5	31	0.1	1.7	1.6	14.7	1.2	26.4
Bee Fork	0.1	0.2	ND	ND	ND	ND	0.2	0.4
West Fork-Black River	0.5	0.7	ND	ND	0.6	1.3	0.9	1.7
Adair Creek	3.6	4.7	1	1.5	ND	0.6	0.5	1
Sweetwater Creek/Tributary	0.2	0.9	0.1	0.5	ND	0.7	ND	ND
Logan Creek	0.2	0.5	ND	ND	0.3	0.8	ND	0.4
Big Creek/Scoggins Branch	4.5	15.1	ND	0.7	1.1	5.1	ND	1.5

Table 14: Drainage area-channel morphology trends for study sites

Channel variable, y (m)	n	Relationship (x= drainage area, km²)	r ²
Active width	62 ^a	y= 3.146 x^0.531	0.691
Bed width	62	y= 2.308 x^0.365	0.635
Bar width	62	y= 0.129 x^1.0366	0.513
Ben width	51 ^b	y= 0.243 x^0.555	0.14
Probe depth	62	y= 0.0041 x + 0.162	0.413
Bar height	62	y= 0.2413 x^0.255	0.306
Bench height	51	y= 0.478 x^0.150	0.124
Bench-fines depth	51	mean= 0.23 m & Cv%= 66 ^c	Х
Bank height (avg)	62	y= 0.743 x^0.166	0.263
Bank height (max)	62	y= 0.865 x^0.208	0.379

^a Two sites omitted (61- Crooked Creek & 95-Adair Creek), no bar deposits

Table 15: Relationship between geomorphic variables and sediment storage

Predictor (x)	Equation ^a	r ²
Active width (m)	y= 0.0524 x^1.812	0.910
Drainage area (km²)	y= 0.347 x^1.006	0.696
Elevation (masl)	y= 1E+20x^-7.737	0.447
Channel slope (m/m)	y= 0.0066x^-1.403	0.313
Valley width (m)	y= 7.865 x^0.153	0.014

^a y= total in-channel sediment storage (m³/m)

^b 11 sites omitted, no bench deposits ^c No relationship with drainage area, sample mean used as best predictor

Table 16: Storage prediction equations for VT streams

No.	Х	Υ	Form	n	R ²	se	se/y%	Fr	bo	b1	p-value
1.	W-photo	W-field	Arithmetic	63	0.755	6.2	26	187.7	2.9950	1.051	<0.000
2.	Wact	Total St	Power	62	0.910	0.154	14	608.2	0.0524	1.812	<0.000
3.	Wact	Bed St	Power	62	0.577	0.254	55	81.7	0.1041	1.092	<0.000
4.	Wact	Bed St	Power	62	0.805	0.329	47	248.1	0.0028	2.464	<0.000
5.	Wact	>WL St	Power	62	0.768	0.367	106	198.2	0.0012	2.457	<0.000
6.	Wact	Ben F St	Power	51	0.210	0.524	neg. y	13.01	0.0114	1.135	<0.000
7.	Wact	Ben C St	Power	51	0.462	0.486	43	42.1	0.0051	1.891	<0.000
8.	Wact	Ben F+C St	Power	51	0.435	0.466	146	37.8	0.0113	1.718	<0.000

Table 17: Total channel storage summary for VT streams

A) Contaminated bulk sediment storage by segment: VT total= 828, 516 m³

	Segment/ID	Bed	Bar	Bench coarse	Bench fine	Total m ³	%
1A	Indian Ck	9,367	17,009	5,266	1,169	32,811	4.0
1C	Indian Ck	3,879				3,879	0.5
2A	WF Crooked Ck	2,151	1,127	591	258	4,128	0.5
2B	Crooked Creek	44,140	136,229	32,635	5,573	218,576	26.4
3C	Strother Ck	26,258	110,230			136,488	16.5
4B	Lick Hollow	1,659	1,967			3,626	0.4
4C	Bills Ck		168,105			168,105	20.3
5A	Adair Ck	5,873	23,735	5,087	748	35,443	4.3
5C	Sweetwater Trib	2,573	3,843	1,239	317	7,972	1.0
5D	Sweetwater Ck	8,210	48,297	9,045	1,061	66,613	8.0
5E	Sweetwater Ck	13,039	57,297	12,233	1,672	84,241	10.2
5G	Logan Ck	10,918				10,918	1.3
6B	Scoggins Br	201	104	54	24	383	0.0
6C	Big Ck	9,726	45,607			55,333	6.7
	Total	137,995	613,549	66,151	10,822		
	%	16.7	74.1	8.0	1.3		

A) Mining-Pb mass storage by segment: VT total= 206.3 Mg

	Segment/ID	Bed	Bar	Bench coarse	Bench fine	Total Mg	%
1A	Indian Ck	0.64	1.60	0.49	0.44	3.17	1.5
1C	Indian Ck	0.54	2.00	01.13	0	0.54	0.3
2A	WF Crooked Ck	1.02	0.40	0.21	2.09	3.72	1.8
2B	Crooked Creek	6.07	21.08	5.05	3.69	35.88	17.4
3C	Strother Ck	2.42	10.33			12.75	6.2
4B	Lick Hollow	6.85	5.86			12.71	6.2
4C	Bills Ck		22.19			22.19	10.8
5A	Adair Ck	5.05	9.32	2.00	8.24	24.62	11.9
5C	Sweetwater Trib	10.04	2.69	0.87	0.17	13.77	6.7
5D	Sweetwater Ck	3.27	25.87	4.85	4.87	38.86	18.8
5E	Sweetwater Ck	2.47	15.62	3.34	1.19	22.62	11.0
5G	Logan Ck	1.99				1.99	1.0
6B	Scoggins Br	0.13	0.09	0.05	0.13	0.39	0.2
6C	Big Ck	0.88	12.26			13.15	6.4
	Total	41.4	127.3	16.8	20.8		
	%	20.0	61.7	8.2	10.1	i i	

Table 18. Comparison of field bar heights and contaminated core depth

	MS	U Study		USGS Bar Core Analysis						
Stream	Site	Bar Ht. ^a	Site & cores	Cont. De	pth ^b (m)	Tot. Sed. Depth ^c	Refusal Depth	Is Cont depth > or		
		(m)		<2 mm	<250 um	(m)	(m)	= Bar ht? ^d		
Indian Ck	46	0.7 to 0.9	IC-FC-1,2,3	0.6 to 0.9	1.2	1.5 to 1.8	3.5	Yes		
Strother Ck	74	0.8								
	75	0.8 to 1.3	SC-FC-1,2,3	0.9 to 2.4 1.1 to 2.4		2.1 to 2.4	3.7	Yes		
	76	0.9 to 1.6								
Bills Ck	80	0.9 to 1.8	BC-FC-1,2,3	0.6 to 0.9	1 to 1.7	2.1 to 2.4	6.4	Yes <250 um		
WF Black R	84	1.3 to 2.7	WF-FC-1,2,3	not conta	aminated-	1.5 to 1.8	2.1	Not sure ^e		
	85	1.7 to 2.3	VVI -1 C-1,2,3	-1101 (01116	aiiiiiateu-	1.5 (0 1.8	2.1	Not sure		
Sweetwater Ck	102	0.3 to 0.6	SW-FC-1,2,3,4	0.3 to 0.9	0.3 to 1.2	1 to 1.8	3.5	Maybe		
	103	1.1 to 1.9	300-1 0-1,2,3,4	0.5 10 0.5	0.5 (0 1.2	1 (0 1.6	3.3			
Logan Ck	100	0.9 to 1.1	LC-FC-1,3	0.6 to 1.2	1.1 to 1.2	1.2 to 1.5	2.2	Yes		

^a Bar heights measured for the sample reach from probe refusal depth in the channel bed to top of bar surface

^b Depth from bar top to where Pb concentration drops below 128 ppm using correction factor of <2 mm ppm Pb x 2.75 = <250 um ppm Pb.

^c Depth from bar surface to top of residuum or refusal, indicates overall thickness of alluvium at coring location.

^d If USGS contaminated depth is greater than MSU bar height, then the assumption that Pb is stored withing the total thickness of channel bars is supported.

^e Field sites do not overlap for this site. The USGS coring site was located 1.6 km and 3.7 km downstream of MSU sites 84 and 85, respectively. No Pb-contaminated sediment was found in the core samples.

Table 19: Comparison of surface and contaminated depth Pb concentration in USGS cores*

USGS Core	Site	Contaminate	ed Depth (m)	Pb (¡	opm)	Avg/Top
Stream	No.			<2 mm sediment fraction		ratio
Stream	NO.	Length	Maximum	Top 0.3 m	Avg depth	Tatio
Bills	1	0.91	0-0.6	78	71	0.90
Creek	2	1.52	0-0.6	113	108	0.95
	3	1.52	0.3-0.9	89	93	1.04
Indian	1	0.91	0-0.6	148	131	0.89
Creek	2	0.91	0-0.3	212	145	0.68
	3	0.91	0-0.6	103	99	0.96
Logan	1	1.22	0-0.3	319	147	0.46
Creek	2	0.91	0.3-0.6	96	124	1.30
	3	1.22	0-0.6	220	237	1.08
Strother	1	2.44	0.3-0.9	77	146	1.89
Creek	2	1.83	0.6-1.2	92	175	1.91
	3	0.91	0-0.3	182	148	0.81
Sweetwater	1	0.91	0.3-0.9	118	127	1.08
Creek	2	0.91	0.3-0.6	72	81	1.13
	3	0.91	0-0.3	79	64	0.81

^{*}The analysis above suggests that the Pb concentration of the surface bar sediment is representative of the average Pb concentration over the entire depth of contaminated bar sediment. Nine of the thirteen bar cores collected by the USGS have the highest Pb concentration in the top 2 ft of the core, with four of these cores having the highest Pb concentration within the 0-1 ft surface layer. The "surface" Pb concentration in the upper foot or 0.3 m of the bar deposit typically ranges from 0.95 to 1.08 times that of the average Pb concentration of the total contaminated depth.

Table 20: Contaminated floodplain soil along streams in the Viburnum Trend

	<2 mm Pl	>345 pp	m in Flood _l	olain Soil	
Stream System	Stream Segment	Leng	th (km)	Vol.	Pb
	(by R-km)	FP soil	FP-CH Dif a	(m³)	(Mg)
Indian Creek	0.8-4.6 & 6.95-9.0	5.9	1.7	7,895	5.6
Courtois Creek	0	0	0	0	0
West Fork-Crooked Creek b	0	0	-2.0	0	0
Crooked Creek	8.35-15.35	7.0	-6.5	38,299	27.5
Left Fork-Neals Creek	0	0	0	0	0
Neals Creek	0	0	0	0	0
Strother Creek	0	0	-5.3	0	0
Lick Hollow Creek	0.0-0.8	0.8	0	1,896	0.9
Bills Creek	0	0	-3.1	0	0
West Fork-Black River	0	0	0	0	0
Bee Fork	14.05-14.5	0.5	0.5	824	0.4
Adair Creek	0.0-1.6	1.6	-0.1	12,204	40.2
Sweetwater Tributary	0.0-1.4	1.4	0.0	10,290	18.2
Sweetwater Creek	0.0-1.45 & 2.6-3.7	2.6	-1.2	39,305	49.2
Logan Creek	0	0	0	0	0
Scoggins Creek	0.0-0.2	0.2	0	3,268	8.0
Big Creek	47.55-49.15	1.6	0	54,208	137.3
Totals		21.5	-16.0	168,189	287.3

^a Difference between contaminated stream length of floodplain soil and channel sediment.

^b Floodplain soils not sampled for Pb along the upper 1.8 km of WF Crooked Creek.

Table 21. Contaminated floodplain width, depth, and volume.

		Active	Total Fl	oodplain S	ediment >345	ppm Pb
Stream	R-km	Width	FP cores	Width	Depth (Avg)	Volume
		(W _{act} , m)	(n)	(m)	(m)	(m³/m)
Adair Ck	0.2	6	1	14.8	0.5	7.4
Adair Ck	1.6	13.7	2	47	0.13	6.1
Sweetwater Ck	0.4	15.1	1	6.4	0.05	0.3
Sweetwater Ck	1	6.3	3	35.1	0.22	7.7
Sweetwater Ck	3.3	17.1	2	152.6	0.2	30.5
SW Tributary	0.3	5	1	49	0.15	7.4
Bee Fork	14.4	32.6	1	18.3	0.1	1.8
Lick Hollow	0.3	3.2	1	15.8	0.15	2.4
Crooked Ck	13.8	8.8	2	122.4	0.13	15.9
Crooked Ck	14.3	4.2	3	34.9	0.2	7.0
Crooked Ck	14.5	3.1	2	3.9	0.3	1.2
Indian Ck	1.2	30.5	3	33	0.1	3.3
Indian Ck	2.3	49.2	1	8.5	0.1	0.9
Indian Ck	7.9	12.7	1	12	0.1	1.2
Big Ck	48	35.1	2	169.4	0.2	33.9
Scoggins Br	0.1	5.6	3	81.7	0.2	16.3

Table 22: Summary of Contaminated Sediment and Soil Storage for VT Streams.

		Channel		F	loodplain			Tota	 al	
Stream	Length	Volume	Pb	Length	Volume	Pb	Volum	ne	Pb)
	km	m³	Mg	km	m³	Mg	m³	FP%	Mg	FP%
Indian Ck	4	36,690	4	6	7,895	6	44,585	18	9	60
WF Crooked Ck	2	4,128	4	none	0	0	4,128	0	4	0
Crooked Ck	14	218,576	36	7	38,299	28	256,875	15	63	43
Strother Ck	5	136,488	13	none	0	0	136,488	0	13	0
Lick Hollow	1	3,626	13	1	1,896	1	5,522	34	14	6
Bills Ck	3	168,105	22	none	0	0	168,105	0	22	0
Bee Fork	none	0	0	0	824	0	824	100	0	100
Adair Ck	2	35,443	25	2	12,204	40	47,647	26	65	62
SW Tributary	1	7,972	14	1	10,290	18	18,262	56	32	57
Sweetwater Ck	4	150,854	62	3	39,305	49	190,159	21	111	44
Logan Ck	5	10,918	2	0	0	0	10,918	0	2	0
Scoggins Br	0	383	0	0	3,268	8	3,651	90	8	95
Big Ck	2	55,333	13	2	54,208	137	109,541	49	151	91
	42.4	828,516	206	21.5	168,189	287	996,705	17	494	58

FIGURES

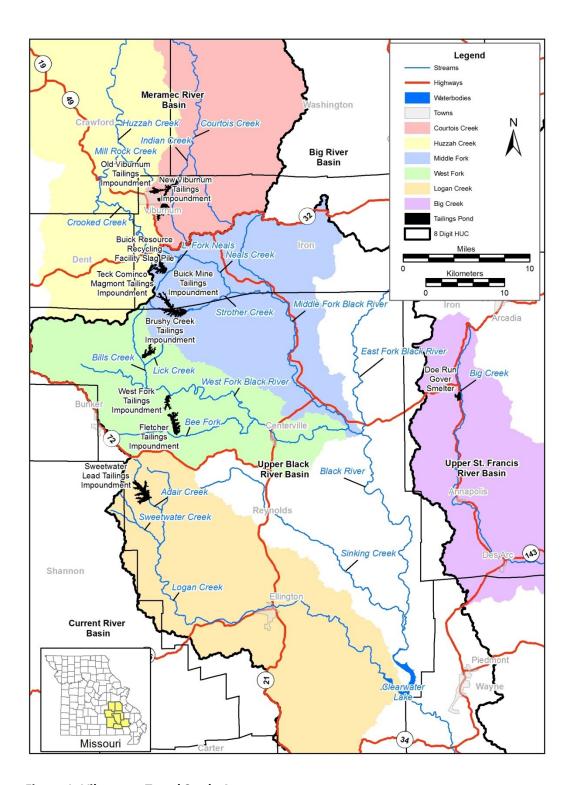


Figure 1. Viburnum Trend Study Area

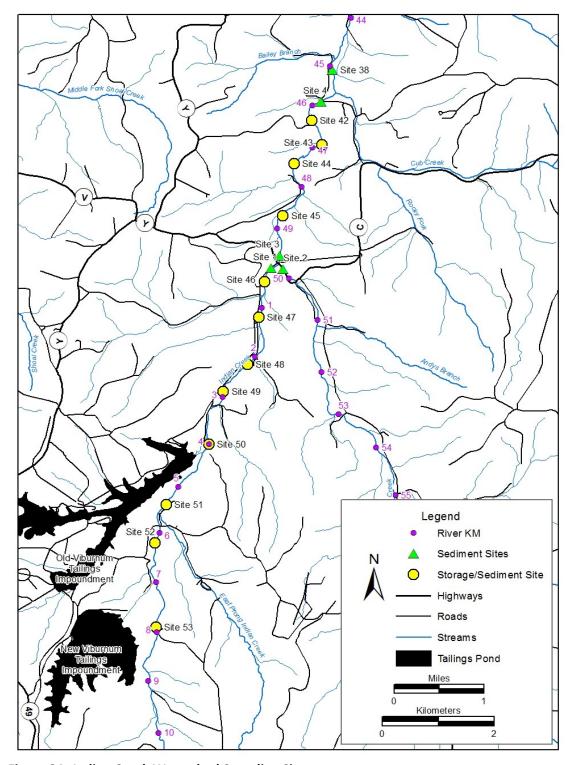


Figure 2A. Indian Creek Watershed Sampling Sites

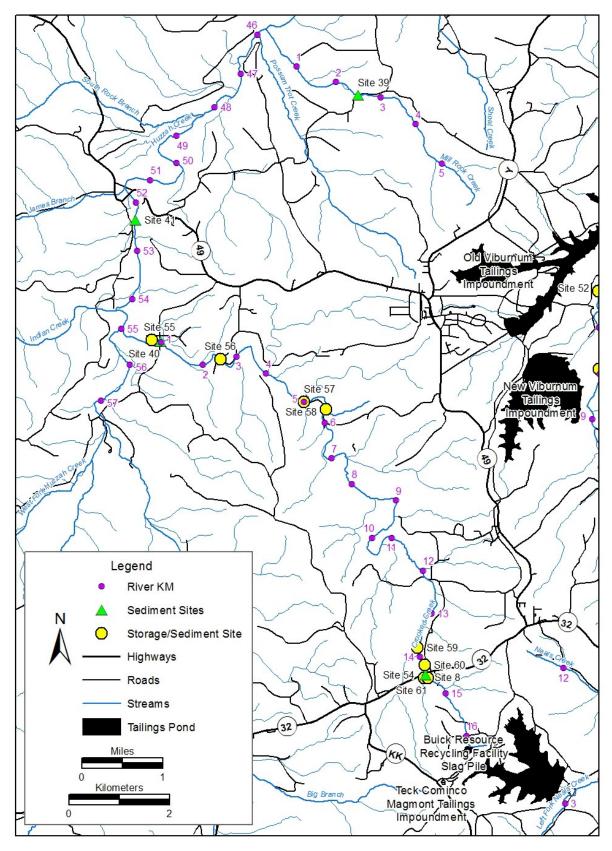


Figure 2B. Crooked Creek Watershed Sampling Sites

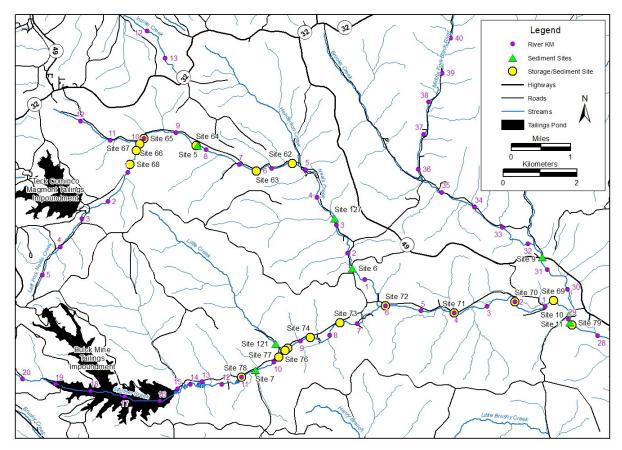


Figure 2C. Strother Creek Watershed Sampling Sites

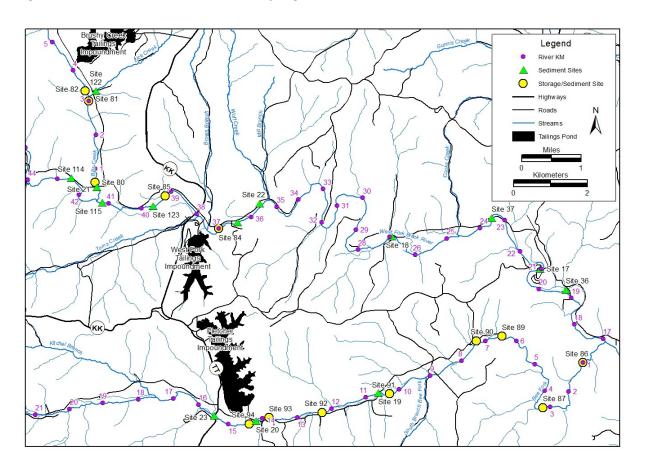


Figure 2D. West Fork Watershed Sampling Sites

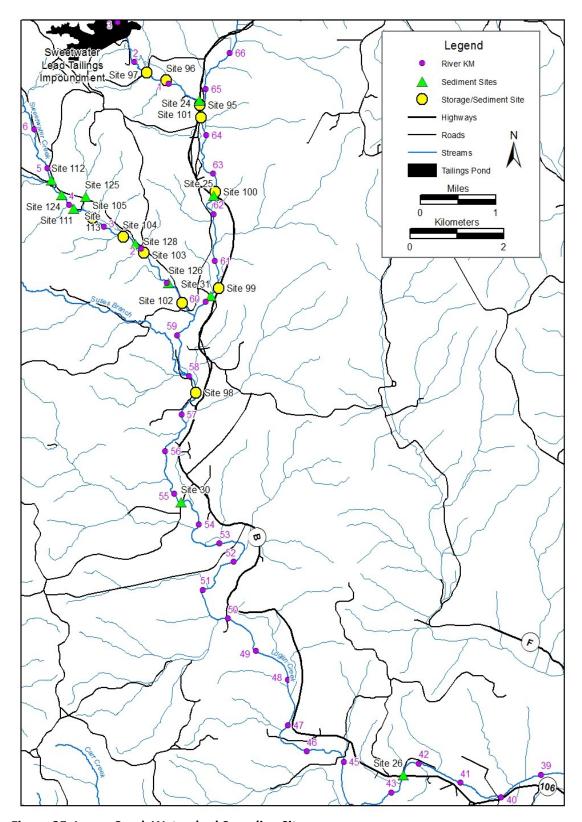


Figure 2E. Logan Creek Watershed Sampling Sites

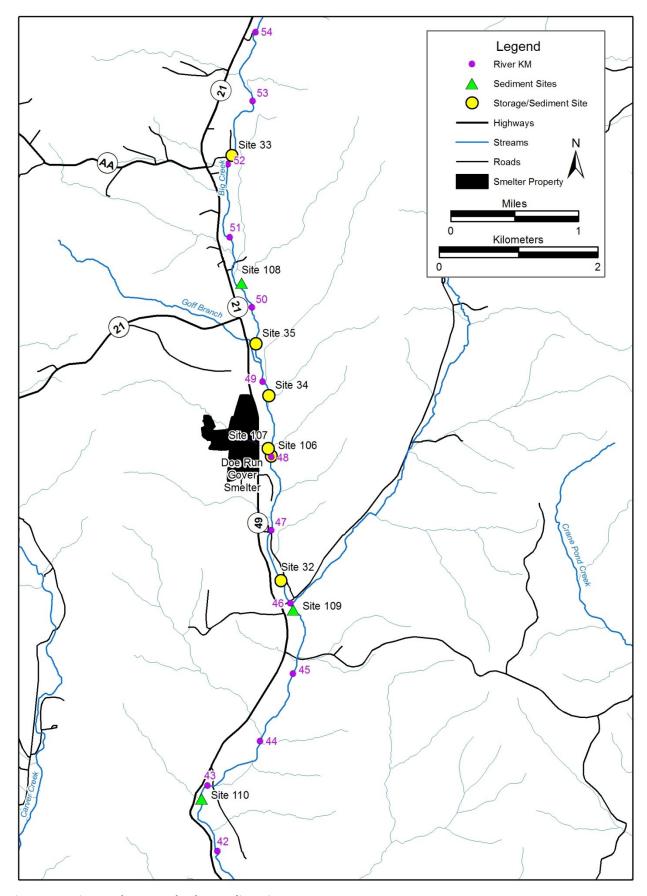


Figure 2F. Big Creek Watershed Sampling Sites

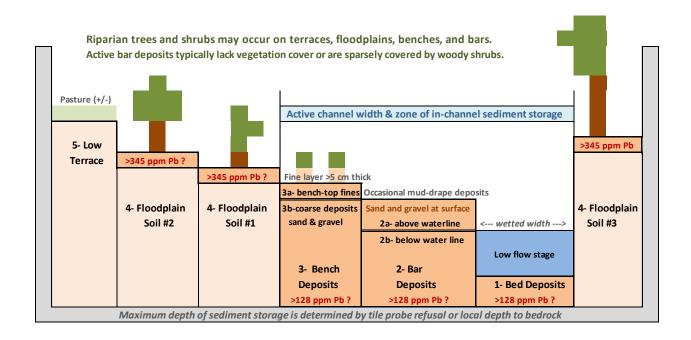


Figure 3. River Sediment Storage Units. This is a schematic diagram of the terminology and relative position of the storage units used in this study and does not represent an actual site. Definitions of each unit are in the text. The active channel width is the distance from bank to opposite bank including all bed, bar, and bench features. Most sites had only had one floodplain for sampling. The maximum number of floodplain units sampled at a site was three.

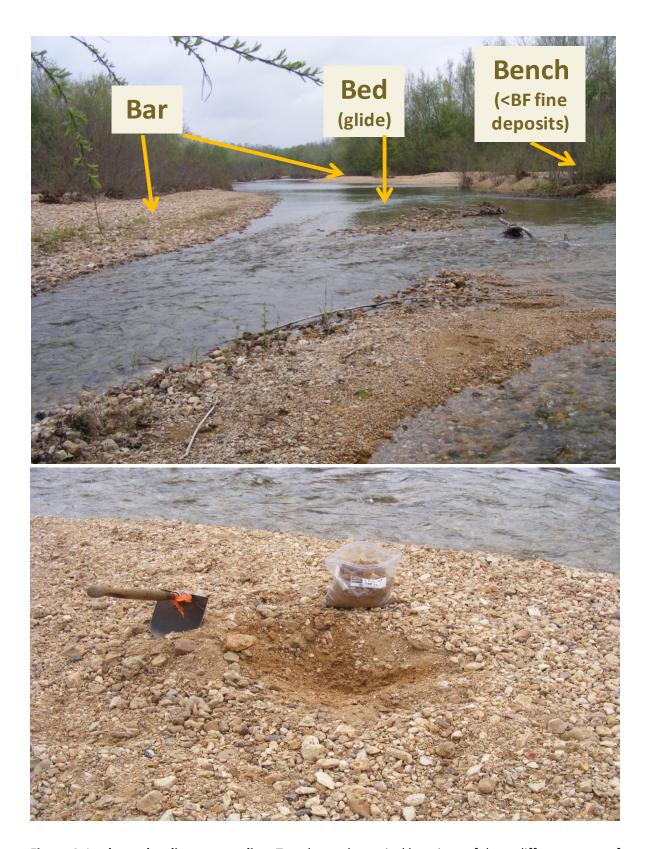


Figure 4. In-channel sediment sampling. Top shows the typical locations of three different types of sediment deposits. Bottom shows the texture of a typical channel bar surface and shallow sample pit with bagged sample ready to be transported to the laboratory. Note the coarser armored layer at on the bar surface and the finer sediment below that is more representative of the bar material as a whole.

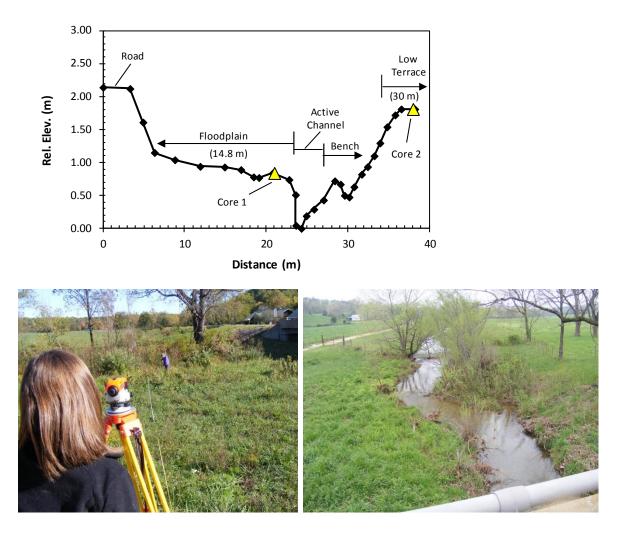
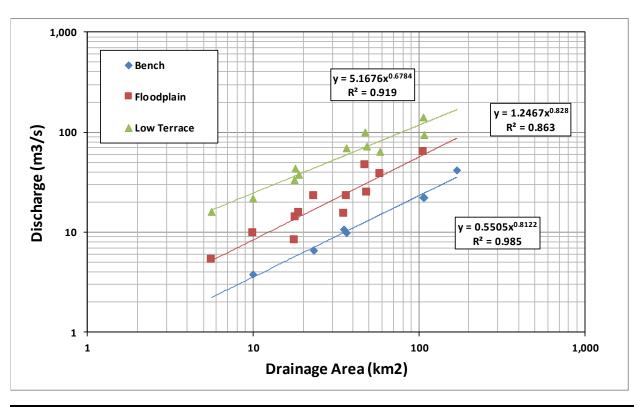


Figure 5. Channel and Floodplain Topographic Surveys and Core Sampling. Top shows a surveyed transect looking upstream and the distribution of mapped alluvial units and core locations for Adair Creek at R-km 0.2 in October 2012. Bottom left shows the surveyed line with auto-level position at distance "0 m" in top figure. Bottom right is an upstream view of the reach in April 2012.



		Drainage	Basin	Bench Stage		Floodplain Stage		Low Terrace	
Stream	R-km	Area	Slope	Discharge	Frequency	Discharge	Frequency	Discharge	Frequency
		km²	m/km	m3/s	RI- yr	m3/s	RI- yr	m3/s	RI- yr
Crooked	13.8	5.6	17.7			5.4	<2	16.1	2-5
LF Neals	0.8	10.0	12.0	3.8	<2	9.9	<2	21.7	2-5
Sweetwater	3.3	17.7	9.8			8.4	<2	32.9	2-5
Adair	1.6	17.9	10.0			14.1	<2	43.6	2-5
Indian	6.0	18.8	10.8			15.7	<2	37.4	2-5
Neals	6.5	23.2	10.8	6.6	<2	22.9	<2		
Bills	3.0	35.2	8.7	10.6	<2	15.4	<2		
Strother	8.7	36.8	6.9	9.9	<2	23.1	<2	69.5	2-5
Big Creek	48.0	47.4	8.83			46.8	<2	100.3	5
Bee Fork	12.3	48.5	8.1			24.9	<2	71.1	2-5
West Fork	39.5	58.7	4.3			38.3	<2	63.1	2-5
Logan	57.6	106.7	5.4	22.3	<2	63.8	<2	140.9	2-5
Courtois	49.5	107.5	6.6	22.3	<2			93.9	2-5
MF-Black	28.8	168.7	7.2	41.8	<2				

Figure 6: Channel morphology and discharge relationships for Viburnum Trend streams.





Figure 7. Floodplain soil sampling. Top shows the typical location of floodplain deposits sampled in 5-10 cm intervals from the surface to the depth of buried gravel deposits. Bottom shows a sample pit on a floodplain.

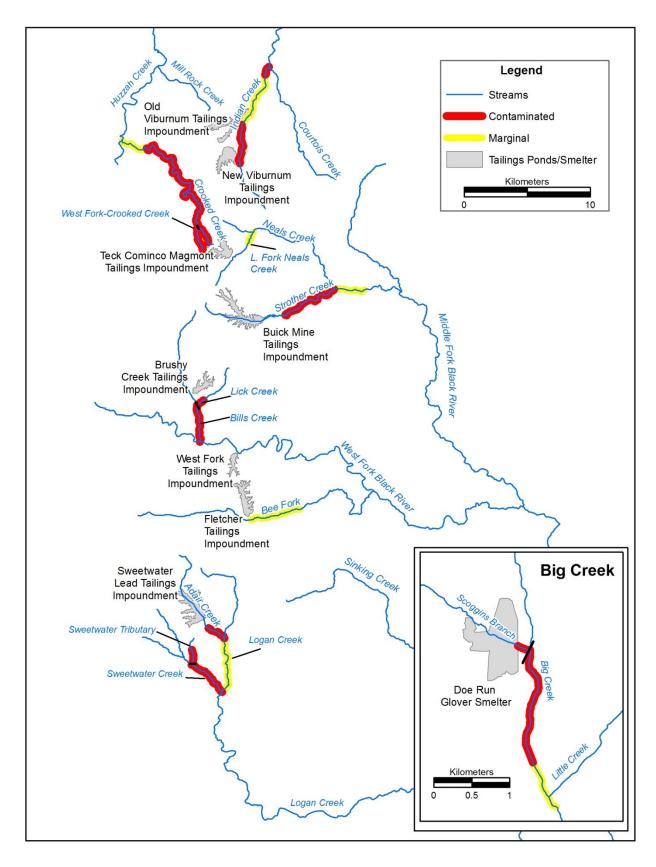
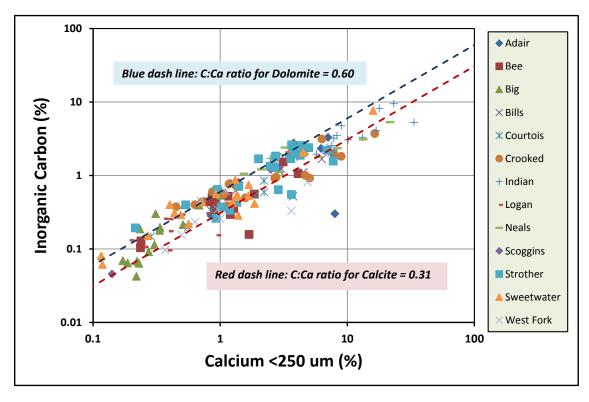


Figure 8: Contaminated and marginal stream segments in the Viburnum Trend.



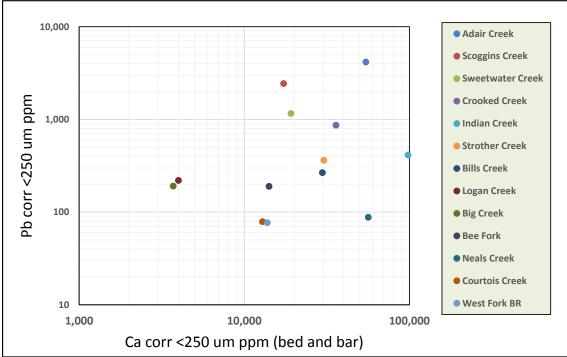


Figure 9. Relationship between calcium and lead in <250 um fraction of channel sediments. Top graph shows that Ca-C ratios in channel sediments fall between dolomite and calcite geochemistry. Bottom graph indicates a weak positive relationship between Pb and Ca. It is expected that mine tailing inputs would contain Bonne Terre dolomite particles with high Pb content (Pavlowsky et al., 2010a). However, the three tailings samples from the Old Viburnum Pond analyzed for this study had relatively low Pb and expectedly high Ca (Table 9)

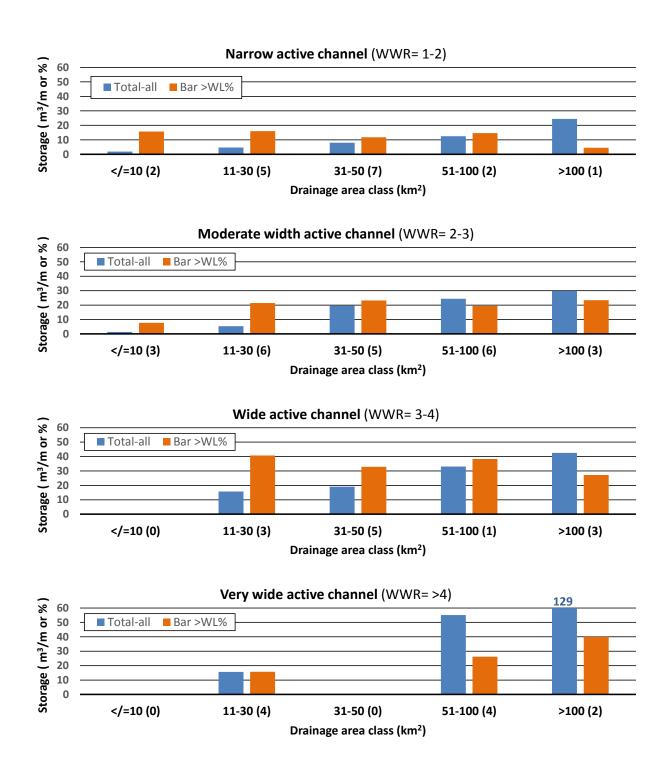


Figure 10: Drainage area and channel width influence on median storage trends. Number of sites in each drainage area class is in parentheses.

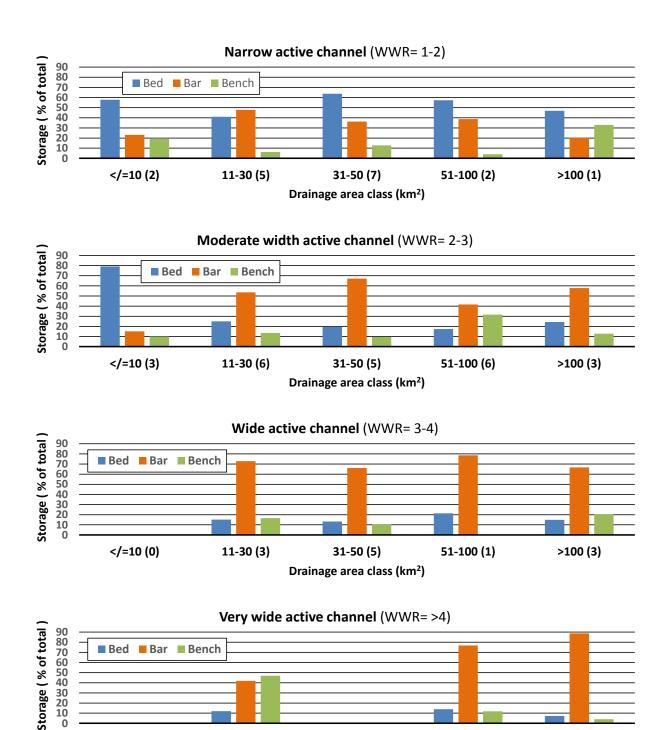


Figure 11: Drainage area and channel width influence on channel storage distribution. Number of sites in each drainage area class is in parentheses.

31-50 (0)

Drainage area class (km²)

51-100 (4)

>100 (2)

11-30 (4)

</=10 (0)

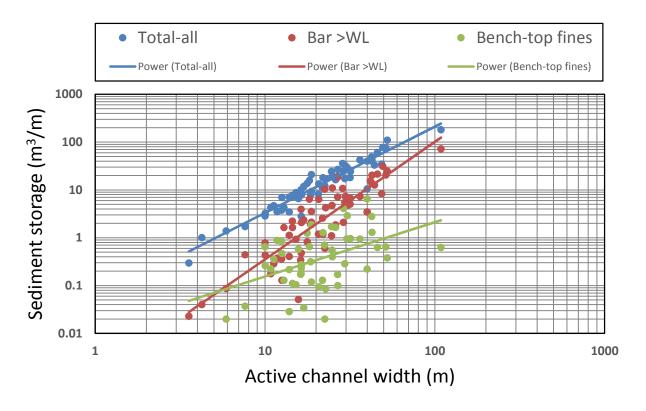


Figure 12: Active width-sediment storage relationships. Regression equations are in Table 16.

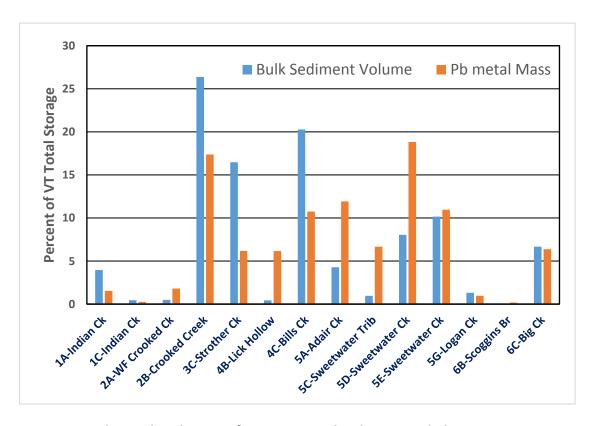


Figure 13. Relative distribution of contaminated sediment and Pb storage.